ISOTOPES AND RADIATION TECHNOLOGY

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION / DIVISION OF ISOTOPES DEVELOPMENT, UNITED STATES ATOMIC ENERGY COMMISSION, by P. S. BAKER, A. F. RUPP, and ASSOCIATES, OAK RIDGE NATIONAL LABORATORY

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ISOTOPES AND RADIATION TECHNOLOGY

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION / DIVISION OF ISOTOPES DEVELOPMENT, UNITED STATES ATOMIC ENERGY COMMISSION, by P. S. BAKER, A. F. RUPP, and ASSOCIATES, OAK RIDGE NATIONAL LABORATORY

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Foreword

Isotopes and Radiation Technology is a Technical Progress Review prepared by the Isotopes Development Center, Oak Ridge National Laboratory, at the request of the Divisions of Technical Information and Isotopes Development, U. S. Atomic Energy Commission. This Review is intended to assist those interested in keeping abreast of significant developments in the fields of isotopes and radiation technology. It is not a comprehensive review of all literature published in this field during a given quarter; rather, it is a mechanism for presenting concise, selected reviews of information on subjects of prevailing Commission interest as it becomes available.

This Review attempts to relate the published results of research and development sponsored by the Division of Isotopes Development to significant developments in radioisotopes and radiation technology, as reported in the world literature. Coverage includes isotope production and development, isotope technology development, isotope applications technology, process radiation development, and radiation processing of food and medical supplies.

In addition to reviews of current literature and special review articles dealing with specific isotopes, facilities, and applications, this publication occasionally contains feature articles prepared by recognized experts on specific topics of current interest. Critical evaluations and interpretations presented are those of the editors and invited reviewers; therefore readers are encouraged to consult the original references in order to obtain all the background of the work reported and the interpretation of the results given by the original authors.

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Section

I

Isotopes and Radiation Technology

Production and Application of Short-Lived Radioisotopes

For the past several years, there has been considerable activity in the production of short-lived radioisotopes, particularly those which can be made in small research reactors. In 1957 Libby,[1] in prognosticating "the emergence of radioisotopes as one of the foremost peaceful dividends from United States atomic investments...," was considering primarily those with half-lives of several years, e.g., 2.65-year Pm^{147}, 5.27-year Co^{60}, 10.6-year Kr^{85}, 28-year Sr^{90}, and 30-year Cs^{137}. However, the shorter lived radioisotopes now appear to have many advantages, and late in 1962 the International Atomic Energy Agency (IAEA) sponsored a seminar,[2] "Production and Use of Short-Lived Radioisotopes from Reactors."

The preparation of this review is to show some of the typical production methods and applications for these isotopes to indicate their potential value. Production and application of these short-lived isotopes are considered in the same light because in most cases the use must follow production very quickly. This results in production and use being essentially a unit operation. Short-lived daughters from radioactive "cows" are also discussed because of their growing usefulness and ready availability. Neutron activation analysis, which was one of the topics included in the 1962 symposium,[2] is not discussed here since the subject was covered in some detail in the Fall 1963 issue of *Isotopes and Radiation Technology*.[3]

The definition of "short-lived" is necessarily arbitrary, but a convenient bracket is from 1 hr to 3 days. Isotopes with half-lives of less than an hour are almost too transitory for processing and practical use. On the other hand, the upper limit of 3 days permits inclusion of the important isotopes Au^{198}, Mo^{99}, and Y^{90}. It should be pointed out that isotopes with half-lives as short as 1 day can be produced in high-flux reactors and shipped anywhere in the world, usually arriving with activities greater (not necessarily at lower cost) than could be made available locally. Yet these isotopes—and more particularly the isotopes with half-lives between 1 hr and 1 day—can sometimes be produced advantageously in the small local research reactors that are now being installed in many countries.

Some of the advantages of short-lived radioisotopes are:

1. Their inclusion broadens the spectrum of isotopes available for general use since often no suitable long-lived species exists.

2. They often can be used for human clinical studies, whereas, in general, the long-half-life nuclides can be used only with animals.

3. Repeated measurements, diagnoses, or therapeutic treatments are possible at shorter time intervals, no corrections for residual activity are required, and radiation dosage to patients is minimized. (Maxfield[4] indicates, for example, that the use of I^{128} instead of I^{131} for thyroid evaluation could cut the delivered dose by a factor of 10.)

4. They may be used in industrial process control or as tracers where longer lived isotopes could not be permitted because of residual contamination.

5. Waste-disposal problems are alleviated if not completely eliminated.

6. Double-tracer techniques become feasible by the simultaneous use of both a short- and a long-lived radioisotope.

7. They may be cheaper than longer lived isotopes since, as is shown later, the production rate is faster, permitting usable amounts of activity to be produced with shorter irradiation times. (This fact enhances the position of the small reactors in the overall production picture.)

In describing the need for short-lived isotopes in their work at Oak Ridge National Laboratory (ORNL), Nelson and Kraus[5] state:

> These short-lived isotopes are useful not only if they are the only ones available for a given element, but also in many other cases. For example, they are often preferred because they can be prepared in high specific activity by short irradiations even if the element bombarded has only a small capture cross-section. Rapidly decaying short-lived tracers can easily be identified in mixtures through their decay rates. Composition and stability of solid materials, for example, inorganic exchangers, may be studied by incorporating short-lived tracers in the materials during preparation; after their decay the materials can be used with other tracers to characterize other properties.
>
> In the past we have tended to avoid isotopes with half-lives of less than a few hours and used them only under special circumstances. However, it appears that in the absence of longer-lived tracers such very short-lived isotopes are still extremely useful for analytic purposes and considerable saving of time may result compared with conventional methods of analysis. Under special conditions, for example in kinetic studies with parent-daughter pairs, isotopes with half-lives as short as a second pose no special complications.

Reactor Production

Isotopes are produced in reactors by two general types of reactions: (1) fissioning of a heavier element (usually U^{235}), and (2) activation, or nuclear rearrangement, of an isotope whose mass is close to that of the desired nuclide. The number of short-lived fission products routinely marketed is limited,[6,7] although many nuclides with half-lives from 1 hr to 3 days (Table I-1) occur in fission-product mixtures in sufficient quantity to be processed and isolated. The chemical separation process is not always simple; further, there are often several isotopes of a particular element, which cannot be separated chemically. Those fission-product isotopes routinely available include 67-hr Mo^{99}, 6-hr Tc^{99m}, 77-hr Te^{132}, 2.3-hr I^{132}, 40-hr La^{140}, 21-hr I^{133}, and 64-hr Y^{90}. For use near reactor sites, others such as 17-hr Zr^{97} might be added.

In contrast, the activation of appropriate targets by any one of several relatively simple neutron-initiated reactions results in a much broader spectrum of radioisotopes, especially if enriched stable isotope targets are considered.[8] Among the suitable reactions for production of radioisotopes by activation, the (n,γ) is the one in most common use at present. Others include the (n,p), (n,α), and $(n,2n)$. The (n,p) and (n,α'), being transmutation reactions, should not be overlooked since, although less efficient, they can give carrier-free products.

Parameters Affecting Activation Yields

The efficiency of a reaction depends on a number of factors, including the flux, cross section, and amount of target material. The activity (in curies) of a radioelement preparation at saturation, A_s, produced by neutron bombardment of a target is given by

$$A_s = \frac{Nf\sigma}{3.7 \times 10^{10}} \qquad (1)$$

where N = number of target atoms (gram atoms of element × % abundance of target isotope × 6×10^{23} atoms/gram atom)
f = flux, neutrons/(cm^2)(sec)
σ = activation cross section, barns
3.7×10^{10} = number of disintegrations per second in 1 curie

Number and Kind of Target Atoms. The quality of the target, especially the chemical and isotopic impurity content, may affect the quality of the product since impure targets often give poor products. "Spectrochemically pure" materials are often far from satisfactory for preparing pure radionuclides since even trace impurities are activated along with the desired target. In at least one instance, spectroscopically pure material has been reported[9] to be even less satisfactory for activations than ordinary chemicals. Chemical impurities usually can be removed, but isotopic impurities are more difficult to handle since the undesirable nuclides cannot be separated chemically. Occasionally very short irradiations can be used, if the irradiation characteristics of the desired and undesired nuclides are compatible. But where natural materials do not provide suitable targets, enriched targets are usually preferable.

For example, suppose that we wished to prepare the pure beta emitter Sn^{121}, with a half-life of 27 hr, from Sn^{120}. The activation cross section for $Sn^{120}(n,\gamma)Sn^{121}$ is 0.14 barn, and its natural abundance is 33%. If natural tin is used as the target, the product is contaminated with other tin isotopes: Sn^{113} from the 0.95% abundant

Sn^{112}, with a cross section of 1.3 barns; traces of 275-day Sn^{119} from the 24% abundant Sn^{118}, with a cross section of 0.01 barn; and 40-min Sn^{123} from 4.7% abundant Sn^{122}, with a cross section of 0.16 barn. However, if a target enriched to 98% Sn^{120} is used, the yield and specific activity of the product are increased by a factor of 3 because of the increased abundance of the target atoms, and the Sn^{113}, Sn^{119}, and Sn^{123} are decreased by factors of ~20, 50, and 20, respectively, because of the depletion of the original unwanted isotopes during the enrichment process. A similar advantage has already been pointed out[10] in this review in connection with the production of Ca^{47}, and numerous other illustrations will become apparent from reference to a chart of the nuclides. Brookhaven National Laboratory (BNL) uses enriched Mg^{26} for production of 21-hr Mg^{28} and its 2-min Al^{28} daughter, as reported by Weiss and Hillman[11] and Stang et al.[27] (see page 212 for a detailed account of the production scheme).

Table I-1 NUCLIDES WITH HALF-LIVES FROM 1 HR TO 3 DAYS WHOSE FISSION YIELD IS SUFFICIENT FOR ISOLATION*

Isotope	Half-life	Fission yield, %
Kr^{87}	78 min	2.7
Kr^{89}	2.8 hr	3.7
Sr^{91}	9.7 hr	5.9
Sr^{92}	2.7 hr	6.1
Y^{90}	64 hr	5.9
Y^{92}	3.6 hr	6.1
Y^{93}	10 hr	6.5
Zr^{97}	17 hr	6.2
Mo^{99}	67 hr	6.1
Te^{132}	77 hr	4.4
Te^{133m}	63 min	4.6
Te^{134}	44 min	6.7
I^{132}	2.4 hr	4.4
I^{133}	20.8 hr	6.5
I^{134}	52.5 min	7.6
I^{135}	6.7 hr	5.9
Xe^{135}	9.1 hr	6.2
La^{140}	40.2 hr	6.3
La^{141}	3.7 hr	6.0
La^{142}	74 min	5.9
Ce^{143}	32 hr	6.2
Pr^{145}	6.0 hr	4.2
Pm^{149}	54 hr	1.3
Sm^{153}	47 hr	0.15

*J. O. Blomeke and Mary F. Todd, Uranium-235 Fission-Product Production as a Function of Thermal Neutron Flux, Irradiation Time, and Decay Time. 1. Atomic Concentrations and Gross Totals, USAEC Report ORNL-2127[Pt. 1(Vol. 1)], (revised Nov. 12, 1958).

Flux

The yields of radioisotopes in neutron activation are, for the most part, related linearly to the flux. However, where secondary reactions are significant because of high cross sections of the initial radioisotope product, high fluxes may actually be a disadvantage since high percentages of the desired product may be burned up. Fortunately, for short irradiations this is not ordinarily a problem.

Most (n,γ) reactions involve thermal (~0.025 ev) neutrons, but the (n,p), (n,α), and $(n,2n)$ are usually fast-neutron (>0.1 Mev) reactions and are sometimes characterized by high-resonance activation cross sections. Dostrovsky and Fraenkel worked out some theoretical production curves for Ca^{47}, showing the importance of neutron energies in optimizing production.[13]

Cross Sections. Although thermal-neutron activation cross sections are published for most potential target nuclides, more information is needed in the areas of neutron resonances and transmutation and $(n,2n)$ reactions concerning the difference between the effects of thermal and fast fluxes.

Yields and Costs. Yields for any activation, as shown by Eq. 1, are directly dependent on the neutron flux; thus, for any given target size and time of irradiation, the quantity of product can be calculated for any particular flux. Therefore any variance from the calculated value means that either the flux was different from that assumed or product was lost during processing. Unfortunately, research reactors are especially noted for flux variations, and identical target samples inserted in the same position in a reactor do not necessarily give comparable yields. Large differences are not uncommon, although 5% variations might be expected if power levels were really "constant,"[14] and result largely from flux depression or perturbation effects of nearby samples and from flux variations representing changes in the fuel loading pattern from time to time.

In general, the shorter the half-life the greater the yield for a given irradiation time. The production equation above gives A_s, the saturation

activity. The activity, A_t, at the end of any shorter irradiation time, t, is

$$A_t = Nf\sigma(1 - e^{-0.693t/T_{1/2}}) \qquad (2)$$

where $T_{1/2}$ is the half-life of the product isotope. It is this relation that makes the economics of the small reactor attractive and sometimes makes it possible to produce a short-lived isotope from a target containing a mixture of isotopes by using very short irradiation times.

Processing losses are minimized by adding carrier or by activating large samples. Decay losses can be reduced only by rapid and efficient handling techniques. Hence proper consideration must be given to the requirements of the user as well as to the difficulties of processing when deciding which isotopes to produce and how to process them. Otherwise the product may be useless or the cost prohibitive.

In many instances, the additional cost of an enriched target is less than the dollars saved by shorter irradiation times and/or increased yield, even with no economic advantage assigned to higher specific activity and absence of undesirable side activities. This is particularly true where transmutation reactions or recoil techniques are involved. The ORNL catalog[6] lists 10 enriched isotopes used as targets in routine isotope production. Although these products are not short-lived according to our definition, the same principles apply.

The range of costs of typical short-lived isotopes can be estimated by the prices currently charged by the various producers. A good listing is contained in *The Isotope Index*,[15] as well as in various catalogs (Refs. 6, 7, and 16–18). The costs can often be lowered considerably by using higher fluxes and enriched targets and by increasing the level of production (which, of course, ultimately depends upon increased customer demand). With short-lived isotopes, inventories are out of the question; thus developing a demand and scheduling runs to coincide with customer needs are both important.

Production Techniques

Nelson and Kraus of ORNL[5] have described the preparation of such isotopes as Na^{24}, Si^{31}, K^{42}, Cu^{64}, Ni^{65}, Br^{82}, and Pd^{109} from neutron-irradiated targets, and Mo^{99}, Te^{132}, and La^{140} from fission products.

By activation of a milligram of appropriate targets in a high-flux [$>10^{14}$ neutrons/(cm^2)(sec)] reactor, they were able to produce several microcuries of active materials in a few minutes. Even with fluxes of 10^{11} neutrons/(cm^2)(sec), more than 0.1 μc (sufficient for many experiments) could be prepared from 0.1 millimole of target in 10 min. With enriched targets, e.g., Si^{30} and Ni^{64}, the yields were increased appreciably, as expected. The irradiations were carried out in "rabbits," inserted and removed by pneumatic or hydraulic devices. Soluble salts (and, occasionally, solutions) were preferred in order to facilitate processing; however, as pointed out by Heydorn,[19] certain target salts such as NH_4Br undergo considerable decomposition during irradiation, and this must be taken into consideration.

Some of the short-lived nuclides required no processing other than dissolution. Others with rigid radiochemical-purity specifications were separated by ion-exchange-column techniques, using both cation and anion resins. For example, 13.6-hr Pd^{109} prepared by irradiation of palladium metal contains 2.7-day Au^{198} from activation of the Au^{197} impurity in the palladium. It can be separated in about 5 min on Dowex 50 because $AuCl_4^-$ is strongly adsorbed on the resin, whereas $PdCl_4^{2-}$ is not. Meinke and coworkers[20–22] have summarized a number of procedures for rapid radiochemical separations.

An unusual scheme is outlined by Nelson and Kraus[5] for processing extremely complex mixtures of fission products. In 4 hr it is possible to separate uranium, neptunium, plutonium, and the fission products into two major groups and then specifically to isolate molybdenum, tellurium, uranium, neptunium, and plutonium. The steps include volatilization of a "volatile group" (e.g., germanium, arsenic, selenium, technetium, ruthenium, and iodine), cation exchange on Dowex 50-X4, and further separation of the sorbed and nonsorbed groups into smaller subgroups and ultimately into individual ionic species by use of Dowex 1 and selective elution.

Aebersold and Rupp, reporting on the production of short-lived isotopes,[23] cite a number of references to earlier publications on the subject. They point out the complementary roles of high-flux reactors and the smaller research reactors. The ORNL facilities are discussed in some detail, including the High-Flux Isotope Reactor (HFIR) with its maximum thermal flux

of 5×10^{15} neutrons/(cm^2)(sec), which is expected to start operation within the next two years. Table I-2, listing a number of (n,γ) isotopes with half-lives of 1.5 to 65 hr, is taken from this report. Rupp has further discussed[24] the short-lived isotopes in connection with the production of high-specific-activity radioisotopes.

Stang[12] has surveyed (57 references) unusual or less frequently used production techniques. He covers many techniques related to reactor activations and evaluates the various consid-

Table I-2 ACTIVATION-PRODUCED SHORT-LIVED ISOTOPES, $T_{1/2}$ = 1.5 TO 64 HR

Z	Product isotope	Half-life, hr	Target atom natural abundance, %	Activation cross section, barns	Specific activity, mc/g [$f = 10^{11}$ neutrons/(cm^2)(sec)]	Specific activity, curies/g [$f = 10^{15}$ neutrons/(cm^2)(sec)]
56	Ba^{139}	1.42	71.66	0.5	4.27	42.7
60	Nd^{149}	1.8	5.72	3.7	2.38	23.8
18	Ar^{41}	1.82	99.6	0.53	2.13	21.3
70	Yb^{177}	2.0	12.73	5.5	66.3	663
66	Dy^{165}	2.3	28.18	1000*	2790	25,100
28	Ni^{65}	2.56	1.16	2.6	0.82	8.2
14	Si^{31}	2.62	3.05	0.11	0.195	2.0
25	Mn^{56}	2.58	100	13.4	390	3,900
55	Cs^{134}	2.9	100	3	36.7	367
71	Lu^{176}	3.7	97.4	35†	318	2,940
30	Zn^{71}	4	0.617			
36	Kr^{85m}	4.4	56.9	0.1	1.09	10
44	Ru^{105}	4.5	18.56	0.7	2.1	21
35	Br^{80}	4.6	49.48	2.9	29.2	292
46	Pd^{111}	5.5	11.81	0.05	0.091	0.9
68	Er^{171}	7.5	14.88	9	13.0	130
58	Ce^{137}	8.7	0.193	6.3	0.14	1.4
63	Eu^{152}	9.3	47.77	1400	7150	59,500
32	Ge^{77}	12	7.67	0.08	0.137	1.4
19	K^{42}	12.5	6.91	1.1	3.17	31.7
53	I^{130}	12.6	50.0‡	24§	152	1,520
29	Cu^{64}	12.8	69.1	4.3	75.5	755
46	Pd^{109}	13.6	26.71	10	41	410
76	Os^{191}	14	26.4	40	91.2	912
30	Zn^{69}	14	18.54	0.1	0.462	4.6
31	Ga^{72}	14.1	34.8	4	37.0	370
11	Na^{24}	15	100	0.54	38.3	383
75	Re^{188}	17	62.93	69	376	3,760
40	Zr^{97}	17	2.80	0.1	0.05	0.5
64	Gd^{159}	18	24.87	4	10.3	103
77	Ir^{194}	19	62.7	130	692	6,920
59	Pr^{142}	19.3	100	10	115	1,150
74	W^{187}	24	28.4	34	85.3	853
80	Hg^{197m_2}	25	0.15	3000	36.4	200
33	As^{76}	27	100	5.4	117	1,170
35	Br^{82}	36	49.48	3.1	31.2	312
56	Ba^{133}	39	0.097	4.1	0.047	0.5
57	La^{140}	40	99.9	8	93.2	93
62	Sm^{153}	47	26	140	394	3,500
48	Cd^{115}	53	29	1.1	4.64	46.4
54	Xe^{133}	55.2	26.89	0.2	0.67	6.7
39	Y^{90}	64	100	1.3	23.7	237
79	Au^{198}	64.8	100	96¶	795	797

*Dysprosium-165 cross section, 5000 barns.
†Samarium-176 cross section, 4000 barns.
‡Radioactive fission product, half-life 1×10^7 years; isotopic abundance from ORNL data, balance is I^{127}.
§Iodine-130 cross section, 18 barns.
¶Gold-198 cross section, 26,000 barns.

erations, including recoil techniques (Szilard-Chalmers reactions). This particular procedure can be quite advantageous when high specific activities are required and the target material has a high target nuclide abundance (making isotopic enrichment of no advantage in increasing specific activity) but a low cross section, or when the available flux is low. The classic example,[25] production of I^{128} from a C_2H_5I target, is cited by Stang for illustration. He also mentions Cl^{36} and Cl^{38} from $KClO_3$. King et al.[26] list some additional Szilard-Chalmers reactions.

At BNL,[12,27] carrier-free Te^{132} (77 hr) is prepared by dissolving aluminum-jacketed uranium-aluminum alloy in HNO_3, catalyzed by mercury. After dilution, the solution is passed over powdered chromatographic alumina, where only anionic tellurium and molybdenum are adsorbed. The molybdenum is eluted with 1*M* NH_4OH, leaving the Te^{132} to be eluted with 3*M* NaOH. Curie amounts of Te^{132} (and, incidentally, Mo^{99}) are available within 5 hr. Stiennon-Bovy and Haegeman-Geladi[28] have also reported on the preparation of Te^{132} and I^{132}, with consideration of the significance of the conditions for production and separation. Barrachina Gomez[29] discusses the preparation of Te^{132} and I^{132} from UF_4 rather than from metallic uranium or uranium oxides.

Stang[12] also describes an indirect tritium reaction for the efficient production of high-purity 2-hr F^{18} by the reactor irradiation of natural Li_2CO_3: $Li^6(n,t)He^4$; $O^{16}(t,n)F^{18}$. A 10-g sample produces ~30 mc of F^{18} after 12 hr in a flux of 10^{13} neutrons/(cm^2)(sec). (Enriched Li^6 increases the yield by a factor of about 10.) After dissolution, the carbonate is passed through a chromatographic alumina column, which adsorbs the F^{18} for later elution with 0.1*M* NaOH.

He mentions the preparation of 21-hr I^{133} from fission products to illustrate the advantage of short irradiation times to enhance production of short-lived isotopes at the expense of longer lived ones. The buildup of 8-day I^{131} is minimized by using a 24-hr irradiation. On the other hand, the 2.3-hr I^{132}, 52-min I^{134}, and 6.7-hr I^{135}, which also are formed, can be allowed to decay for about 30 hr to reduce the extraneous iodine content to a tolerable level.

Magnesium-28 (21 hr) is made at BNL (Refs. 5, 11, 12, and 27) by reactor irradiation of thin foils of a Li^6-Mg^{26} alloy at a flux of 10^{13} neutrons/(cm^2)(sec) for 3 days, taking advantage of the $Li^6(n,t)He^4$ and $Mg^{26}(t,p)Mg^{28}$ reactions. The use of enriched lithium and magnesium targets increases the product activity 10- and 30-fold, respectively. The irradiated foils are dissolved in water; the $Mg(OH)_2$ that forms is centrifuged off, washed with water, and dissolved in HCl; and the solution is passed through chromatographic alumina and Dowex 1 anion-exchange resin. About 40 mc of Mg^{28} is recovered in 2 to 3 hr.

Milkers

Stang[12] and Stang and Richards[30] also describe a number of "generator" or "milker" isotopes produced at BNL (see also the Winter 1963–1964 issue of *Isotopes and Radiation Technology*[31]). For example, 2.3-hr I^{132} can be obtained repeatedly from Te^{132} adsorbed on alumina in what is called an "isotope generator." Elution with 15 ml of 0.01*M* NH_4OH requires only 5 min and gives a product with <0.001% radioactive tellurium and (if eluted daily) <0.3% I^{131}.

Similarly, 6-hr Tc^{99m} can be milked from Mo^{99} (mentioned above) adsorbed on alumina by elution with 0.1*M* HNO_3 or HCl. Yttrium-90 is eluted from Sr^{90} adsorbed on Dowex 50W-X8 cation resin by passing 0.5% citric acid at *p*H 5.5 over the resin. Aluminum-28 (half-life 2.2 min) is made available by eluting it with 1*M* NaOH from its parent Mg^{28} (mentioned above) adsorbed on Dowex 50W-X8.

Frühauf[32] described a Ba^{137m} generator suitable for delivering the activity in an organic solvent. The Ba^{137m} is extracted into a 0.05*M* solution of thenoyltrifluoroacetone in acetophenone containing 20% of a hydrocarbon diluent of boiling point 200°C. In addition to the Cs^{137} activity, the aqueous phase contains 1 mg of cesium per milliliter as holdback carrier, 10% NaCl to increase the specific gravity, and borate buffer to hold the *p*H at 9. Contacting with an equal volume of extractant yields 70% of the gamma activity in the organic phase with <1% Cs^{137} contamination.

Special Facilities in Reactors

Taylor, West, and Whiting[33] discuss the general problems in the United Kingdom relative to the production and distribution of short-lived isotopes, without covering any specific nuclides. In their BEPO reactor they use a sample

changer operating on the endless-belt principle and have found it thoroughly satisfactory for an isotope program in a large graphite-moderated reactor. The belt, a flexible chain of 300 sample holders, passes directly across the reactor core. Figure I-1 shows the details of the control head for introducing and removing samples. Aluminum-28 activity from the aluminum sample container amounts to as much as 4 curies per container if the samples are withdrawn from the center of the reactor directly to the operating head. This is ordinarily dealt with by allowing the samples to decay for a few minutes in the biological shield of the reactor before unloading. The utility of this system is pointed up by the fact that gold grains for medical use can be irradiated up to 4 hr and shipped on the same day that an order is received.

The high-flux DIDO reactor uses a flexible system with 10 cylindrical magazines mounted one behind the other on a central shaft and a keying mechanism that allows independent rotation (Fig. I-2). Each magazine has seven chambers in which the 30-cm^3 isotope cans lie horizontally. The cans are blown individually into the desired irradiation position by CO_2 and are subsequently returned through the same passage for unloading.

Meinke[34] reports on the processing of radioisotopes with half-lives from minutes to a few

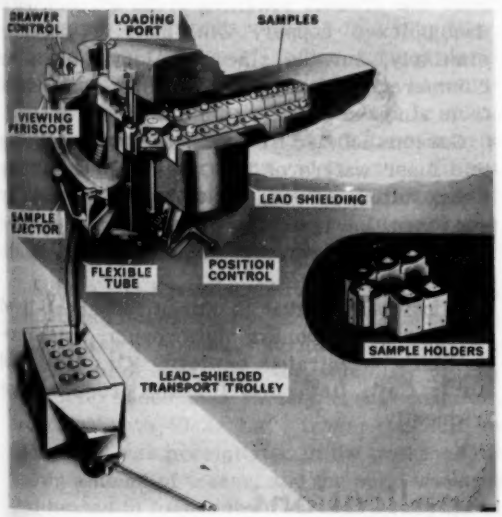


Fig. I-1 Detail of control head for belt type irradiation equipment.

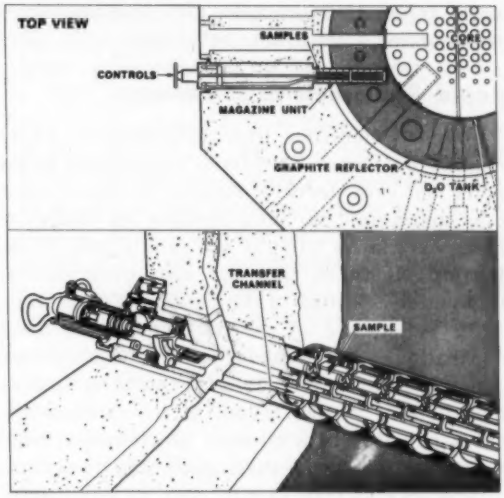


Fig. I-2 Magazine type irradiation equipment installed in DIDO.

hours, which have been produced in a 1-Mw university research reactor. He notes: "To exploit short-lived isotopes it is not essential to have large stocks of isotopes, nor three-shift reactor operations, nor elaborate processing facilities." The heart of the system he describes is a reactor–pneumatic-tube facility,[35] which transfers samples from reactor core to a laboratory hood in 3 sec. Present cost for such a facility is probably less than $15,000, and he terms it "indispensable."

Greendale and Love[36] have modified a rabbit to allow rapid transfer of irradiated solutions from it to a container for fast radiochemical separations. After irradiation, the device is transferred from the reactor through a pneumatic tube to a receiver where it impales itself onto two hypodermic needles connected to an evacuated container. Within 2 sec, the irradiated solution and one acid rinse are quantitatively transferred to the container for processing. The system is completely contained so that there is no danger to personnel or of contamination of the laboratory.

Obviously, rapid-measuring equipment is also necessary as part of the processing. For "clean" samples, gross decay measurements are suitable; continuous recording on printing scalers allows still more flexibility. But the most satisfactory equipment is some type of multichannel pulse-height analyzer—preferably able to re-

cord information rapidly and continuously—with gamma scintillation detectors.

Rapid Radiochemical Processes

Meinke[34] indicates that radiochemical processing techniques have been streamlined to the point that even peroxide fusions in nickel crucibles and acidic or basic leaches for biological samples can be carried out in a minute or so, leaving plenty of time for subsequent decontamination and use of the isotope. Fortunately, 100% yields are of no consequence in these separations, so procedures can be shortened considerably. On the basis of reports by Sunderman et al.[37–39] and DeVoe[40] on the radiochemical separation of a number of elements, most radiochemical separation steps can be accomplished in less than 15 min. And, as was pointed out earlier, with the help of ion-exchange techniques—and also with solvent extraction—even the most complicated separations can be completed within 30 min to a few hours.

On the other hand, Meinke intimates that, for routine operations, one-step separations of a particular isotope can often be worked out to advantage: "It is definitely possible to make separations routinely on all types of samples on time scales of a few minutes." Table I-3 lists some typical isotopes and indicates how they are separated, with appropriate references.

Recently Rengan and Meinke[49] have worked out procedures for separations of various activated rare earths in 10 to 16 min, using Dowex 50W-X12, −100 mesh, cation-exchange resin. For rare earths differing by three or more atomic numbers, with α-hydroxyisobutyric acid as eluant, good separation is accomplished in 10 min. With adjacent rare earths, less complete but usable amounts of activity are obtained in about 16 min. Such isotopes as 2.0-hr Yb^{177}, 2.3-hr Dy^{165}, 9.2-hr Eu^{152m}, and 19.1-hr Pr^{142} were studied.

Table I-3 TYPICAL SHORT-LIVED RADIOISOTOPES SEPARATED RADIOCHEMICALLY

Isotope	Half-life, min	Separation method	Reference
Ag^{108}	2.3	Chloride precipitation or AgCl exchange	41,42
Co^{60m}	10.5	Oxine extraction plus reduction to metal	43
Cu^{66}	5.2	Zinc dibenzyl-dithiocarbamate extraction	44
Rh^{104m}	4.4	Pyridine extraction	45
Se^{79m}	3.9	Diisobutyl ketone extraction	46
Ti^{51}	5.8	Cupferron extraction	47
V^{52}	3.8	Cupferron extraction	48

In discussing the 50-kw TRIGA reactor being used by the Lovanium University, Leopoldville, Congo, for isotope production, Loos[50] explains that they have no facilities for chemical treatment of highly active substances; hence, target samples for high-level irradiations must necessarily be in a suitable chemical form for simple processing (e.g., Na_2CO_3, K_2CO_3, and $CuCl_2$ or $CuSO_4$). For low-level products, ion-exchange purificiations are used, with, for example, Amberlite-400R for separating molybdenum.

Felix et al.,[51] in discussing short-lived isotope production at the Hahn-Meitner Institute in West Berlin, indicate that Na^{24}, K^{42}, and Au^{198} are produced by the traditional procedures but that Cu^{64} and Zn^{69m} require unusual techniques. Copper-64 is produced by the usual Szilard-Chalmers method from copper phthalocyanine. But, after a 2-hr extraction of the Cu^{64} in boiling $2M$ H_2SO_4 (containing 1 ml of octanol as a wetting agent), a new method for purification of the isotope is used, in which the copper is separated from organic radiolytic decomposition products by overnight electrolysis. The resulting Cu^{64} is 500- to 1000-fold enriched over the product resulting from irradiation of uncomplexed copper. Zinc-$69m$ is produced similarly, but the zinc phthalocyanine is not commercially available and must be synthesized from zinc and phthalic acid dinitrile.

Gaseous labeled HF^{18} is made by irradiating thin fused wafers of $LiNO_3$ and coprecipitating the resulting F^{18} with $BaSO_4$. The solid product can then be treated with CaF_2 carrier and H_2SO_4 to liberate HF^{18} when and where the customer needs it.

Kim[52] reports that in Korea the short-lived isotopes are becoming quite popular, with production concentrated on Na^{24}, K^{42}, Mo^{99}, and Au^{198}; Cu^{64}, Br^{82}, and I^{128} are produced less frequently.

Applications

The applications of short-lived isotopes are numerous. Some are novel, and some simply

represent substitution of short-lived for long-lived nuclides in routine applications. They include such areas as tracing liquid flow and gas and liquid leaks, kinetic studies, evaluation of carbon papers, industrial process control, and medical diagnoses. For example, Erwall et al.,[53] in a review of 28 references, discuss the use of several isotopes (Na^{24}, Cl^{38}, K^{42}, Mn^{56}, Br^{82}, La^{140}, and Au^{198}) in the following typical examples of uses in industry (especially Swedish): (1) studies of solid transport through process units, e.g., bleaching towers, Dorr thickeners, cellulose digestors, blast furnaces, and rotary kilns; (2) measurement of flow rates for liquids in tubes and open streams; (3) estimation of residence times and holdback and blocked volumes for liquids in various process units, as in the paper industry; (4) determination of the amount of slag in open-hearth furnaces through "weighing" by isotope dilution; (5) studies of the origin of nonmetallic inclusions in steel to find better lining materials and improved pouring techniques; (6) labeling for positive identification in quality control for the steel industry; (7) determination of the efficiency of mixing in the concrete industry; (8) detection and localization of leaks; (9) plotting of flow patterns in receivers for sewage or waste water to find the best outlet for such liquids.

Basic Research

Adloff and Adloff-Bacher[54] report the labeling of organic compounds with 2.3-hr I^{132} by taking advantage of "nascent" iodine formed during the decay of the parent Te^{132}. (The reactivity comes partly from the sudden change in atomic number during decay and partly from internal conversion of the gamma ray following the beta emission.) Dissolving $Te^{132}Cl_4$ in an organic liquid to be labeled makes it possible to prepare high-specific-activity species very rapidly.

Nelson and Kraus[5] and Kraus et al.[55] report the use of short-lived isotopes for rapidly measuring solubilities of sparingly soluble salts tagged with tracers. For example, the solubility of LaF_3 was determined in a variety of HF-containing solutions with 40-hr La^{140} tracers as follows: The LaF_3 was precipitated in the presence of a known amount of tracer, and the solid was dried and heated to form anhydrous LaF_3. Solubilities were determined by passing the test solution through a bed of the LaF_3 crystals and relating the steady-state counting rate of the effluent solution to the original count-to-weight ratio of the solid. Figure I-3 shows the results of solubility measurements, at 50 and 70°C, for LaF_3 in HCl-$HClO_3$ mixtures of constant molarity. Similar measurements on the solubility of LaF_3 in $9M$ HCl–$0.1M$ HF as a function of added H_3BO_3 concentration showed a marked increase in solubility with increasing boric acid concentration. This type of measurement lends itself nicely to studies of complexing reactions.

These investigators also used short-lived isotopes to study ion-exchange phenomena in

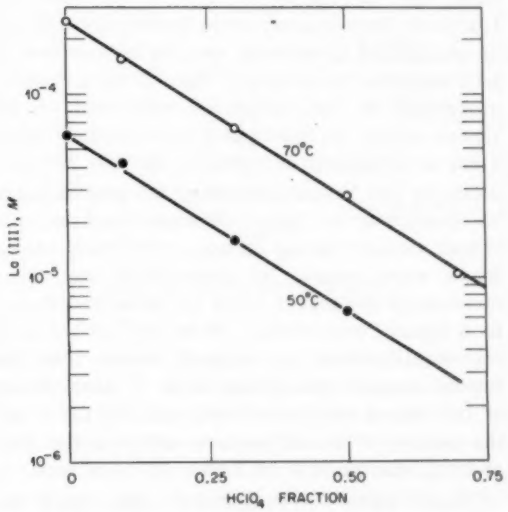


Fig. I-3 Solubility of LaF_3 in $8.9M$ ($HClO_4$ + HCl) mixtures at constant $0.102M$ HF.

different media to obtain information on complexing behavior of the elements[56] and properties of the ion-exchange materials.[55] Results of such studies frequently point the way to suitable separation methods. By examining decay rates of elution bands containing short-lived tracers, they were able to simplify the analysis of rather complicated mixtures. The procedure is further enhanced by selection of appropriate parent-daughter pairs, which alleviates some of the inconvenience associated with the use of short-lived isotopes.

One of the very earliest uses of radioisotopes was in the measurement of diffusion.[57] Some of the early work was reviewed by Wang.[58] Nelson and Kraus[59] in their diffusion studies tried to use or devise tracer methods that are rapid,

yet reasonably precise. A modification of the shallow-bed ion-exchange techniques,[60,61] used at constant temperature, comprised (1) equilibration of the tracer with resin beads of uniform radius; (2) preparation of a shallow bed of beads, usually about 1 mm deep, with the beads supported in a tube on a fine-mesh platinum gauze, glass wool, or frits (or porous Teflon if HF is involved); (3) establishment of the initial counting rate through a slit in a lead shield; and (4) rapid washing of the bed with equilibrium solution but without tracer. The activity of the bed during elution is plotted as a function of time, and, as long as the flow rate is rapid, the tracer is flushed away from the beads as rapidly as it diffuses from them and can be assumed to be controlled by diffusion. The diffusion is characterized by the diffusion coefficient of the tracer within the beads, and the diffusion coefficient is ultimately determined directly from the slope in the linear portion of the plot of log of concentration vs. time. (If significant decay of tracer occurs during elution, correction can be made very simply by subtracting the decay constant of the tracer from the observed slope.) In a typical experiment, 36-hr Br^{82} in 1*M* LiCl was equilibrated for several hours with the ion-exchange resin Dowex 21K. A shallow bed of the beads was then eluted with 1*M* LiCl, and the value of the diffusion coefficient for Br^{82} at 25°C was found to be 1.52×10^{-6} cm^2/sec.

These same investigators[5] also used the porous-frit technique developed by Wall et al.,[62] in which a slab of porous material is saturated with solution containing tracer, and then identical solution, but without tracer, is passed through the porous medium. The diffusion coefficients of Br^{82} in HCl, LiCl, and benzyltrimethylammonium chloride solutions were measured for a wide range of concentrations for determining to what extent concentrated electrolyte solutions can serve as models for ion exchangers.

In Korea, Kim[52] reports that the kinetics of the exchange reaction between gallium bromide and ethyl bromide have been studied with radioactive gallium bromide dissolved in an organic solvent.

Industry

Frühauf[63] has discussed the use of short-lived isotopes in the evaluation of performance characteristics of chemical production plants. For example, La^{140} has been used to evaluate the efficiencies of various weirs and shovels, and the influence of grain size on particle migration, in a rotary kiln used for roasting pyrite. The same isotope has also been used as a core in coke pellets to indicate circulation time in a crude-oil cracker, where the coke pellets served as a heat-transfer medium.

Frühauf also reports a study of liquid flow using La^{140}, Na^{24}, or Mn^{56} sealed in a hollow polypropylene sphere. The density of the sphere is adjusted with lead shot, and the sphere is sealed by heating and placed in the liquid whose flow is to be traced. The activity is then followed with suitable detection equipment.

Bjerle[64] has described the benefits of short-lived isotopes in studying the mixing of powders. In the preparation of lightweight concrete, thorough mixing of the cement, sand, aluminum powder, and water is necessary to obtain a high-quality product. Optimum mixing in a minimum of time is required so that the reaction between the aluminum powder and water, which is responsible for the characteristic structure of the product, does not occur inside the mixer. The efficiencies of several different designs of mixers have been studied with 2.6-hr Mn^{56}, from a manganese impurity in commercial aluminum powder, and with Na^{24} and K^{42}, from the irradiations of aluminum and cement, respectively. The theoretical aspects of the technique are also evaluated. Forsberg and Bjerle[65] reported earlier on the mixing efficiencies of other cement-sand mixing devices.

An interesting indirect method for tracing powdered materials for physical transport studies is described by Petersen.[66] Some of the material to be used is slurried in water (if insoluble) or in ether (if soluble in water), and a solution of stannous chloride is added. After standing for 5 min, the slurry is filtered or centrifuged and washed to remove excess $SnCl_2$. Gold-198 solution is then added to the suspended solid, and the gold is reduced quantitatively on the surface of the material. Only 1% of the gold could be removed in washing and shaking experiments, making it suitable for powder mixing studies.

A valuable application of Br^{82}, as reported by Watt,[67] is for the detection of gas leaks in pipes from gas mains. It is estimated that between 10 and 20% of Australia's gas consumption is lost through leaks that cannot be located for

want of a suitable method. The present technique involves adding 500 μc of CH_3Br^{82} under pressure to the individual service pipe and locating leaks by the increase in gamma-ray intensity where the activity escapes into the soil. It is claimed that such leaks can be located to within 6 in. About 90% of the methyl bromide can be recovered for reuse.

Tellier et al.[68] describe the applications of short-lived isotopes in the French gas industry. A rather intriguing use involves a study of "fogging" oil suspended in fuel gas to condition the rubber joints in the gas distribution pipes. When these conditioners are added in quantities above saturation, they appear as fogs; these aerosols are moved by the gas and deposited on the pipes and joints up to a certain distance, called the "fog range," which actually is a measure of the efficiency of the fogging apparatus. Labeling the oil with Br^{82}-bromonaphthalene has provided a very sensitive method for evaluation of the system.

Tellier also discusses the use of Na^{24} in locating gas leaks in transmission pipelines prior to placement in service. All gas transmission lines are subjected, before being put in service, to a test of mechanical resistance to water, in the course of which all leaks must be detectable. The pipeline is marked from the outside by a series of Co^{60} sources. Water under pressure and containing Na^{24} is driven through the pipe by a column of pure water. About 1 km behind the radioactive solution, and in the pure water, a detector with a magnetic wire recorder is introduced into the pipeline, drawn by a tight-fitting piston. At the end of the pipeline, the detector and recorder are removed, and the wire is unwound in a recording reader, which furnishes a graph. It is possible to detect through the pipe wall any Na^{24} that has leaked into the soil (25 to 50 μc per leak) by locating signals that are abnormal in comparison with the regular and expected peaks of the Co^{60} (Fig. I-4). This testing is done on 20-km sections of pipe at a time.

For in-service detection of leaks in gas mains, CH_3Br^{82} is added to the distribution system to supply a "radioactive wave" through the system. Leakage rates >15 liters/hr can be detected by externally sensing the Br^{82} activity (~1 mc) released through the leak during the passage of the wave. Although the technique is less sensitive than a procedure in which the gas is homogeneously labeled, it has the advantage that service to the customer has to be cut off only during the passage of the wave.

Industrial boiler-water studies with Na^{24} have been described by Maille et al.[69] Conventional methods for studying circulation inside an industrial boiler are complex and often disturb the phenomenon under study. The circulation depends on the flow rate and the specific gravity of the water-steam emulsion. In cases where an external source (such as Co^{60}) and a detector[70,71] are unsuitable for densitometry measurements, the addition of a calculated amount of Na^{24} to the boiler water does not disturb the flow and gives consistent values for the specific gravity. Detectors are placed at the bottom and at the top of the screen tube. By appropriate calculations, the activity at the bottom of the tube (which contains water alone) is related to the activity at the top of the tube (which contains a water-steam emulsion) so as to obtain the specific gravity of the water-steam emulsion.

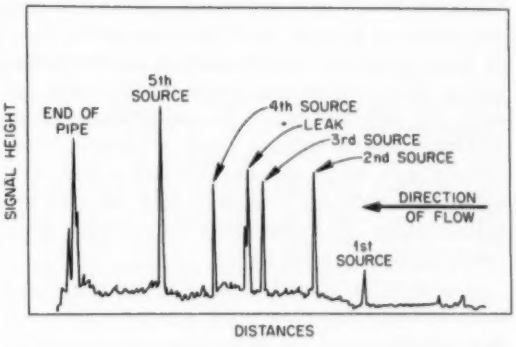


Fig. I-4 Recording of a leak.

Akerman et al.[72] describe an investigation of the fundamental principles involved in zinc redistillation, showing how Cu^{64}, Fe^{59}, Cd^{115}, and Zn^{69m} have been used to evaluate the purification process and to substantiate the theory proposed by Krupkoroski et al. (referenced by Akerman). The tracers made it possible to investigate such things as the separation of the components at selected points in the rectification column and to determine the time that zinc remains in the column.

Sodium-24 has also been used to study longitudinal turbulent diffusion in columns of liquids by injecting the isotope at the top of the column and measuring the activity at various positions along the column as a function of time.

Water Flow

Kim[52] indicates that the principal use of Na^{24} in Korea is for the detection of leaks in irrigation-water storage containers; there are ~1500 such containers in South Korea alone.

Iodine-131 has been used in the past in Australia for tracing water flow.[73] More recently, with the advent of local production of isotopes, Au^{198} has replaced I^{131} with the advantages that high activities are available at low cost, its 2.7-day half-life is about the length to time required for completion of most tracer tests, and it can be used to label solid materials such as silt and sand by adsorption. In one instance where effluent from a proposed pulp factory was to be discharged into a bay, a 5-curie test with Au^{198} showed that the bay was self-flushing and hence that the effluent would not accumulate in the bay.

In a similar manner, Berg and Somer[74] determined suitable places for sewage-water outlets into the open sea in localities where pollution of bathing beaches, fishing harbors, and fishing waters could occur. Their studies extended the techniques using Br^{82} and Na^{24} (Refs. 75 and 76) for flow tests to provide a method for further treatment of the information in order to give the required quantitative figures of the distribution of sewage concentration. Bromine-82 is introduced into the sea at the location being considered for an outlet. Activity measurements are taken from a boat that takes a zigzag course through the whole area covered by the radioactive solution. Position, time, and count rate are automatically recorded. Plots of isoactivity curves and data for the variation in count rate with time for as many points as are necessary permit charting the expected distribution of waste-water concentration. Ultimately, from a time-activity coordinate system, the expected concentration of waste water can be calculated and isoconcentration curves drawn.

In another case, 300 mc of Au^{198} showed that there was no buildup in effluent that was being discharged from a sulfide works into a small creek. In a third experiment, 50 curies of Au^{198} adsorbed on 100 lb of fly ash was used as a tracer for 250 tons of this ash being dumped in the ocean. It was found that ocean currents soon dispersed the ash and carried it out to sea.

Gaspar et al.[77] report on the use of La^{140} and Na^{24} to study the direction and flow velocity of subterrranean waters through a sandy medium, rich in organic material, adjoining the Black Sea. Although Br^{82} and I^{131} are generally the best tracers, the La^{140}-Na^{24} mixture was used simply because it was readily available and would not be adsorbed by the nonargillaceous soil. The isotope mixture, containing about 30 mc in several liters of solution, was slowly introduced into a central well about 1 m below the surface of the subterranean water. The passage of the activity through other surrounding wells (1 to 5 m apart) was followed by submersible Geiger-Mueller counters. It was found that the flow was south to north at a velocity of about 0.6 m/day (18 to 20 m in 30 days). This was completely inconsistent with a hypothesis concerning the industrial pollution of a fresh-water lake in the vicinity of the tests.

Guizerix and Cornuet[78] have also reported on water leak detection with Na^{24}. The usual technique of labeling the water in the system and then draining the water and detecting residual activity in the vicinity of the leak has certain shortcomings, including the possibility that the marked water below a leak in a water main may be carried off along the main or the possibility that some radioactive water may remain in a low place in the water main. These investigators follow the progress in time of any abnormal spot of activity, during introduction of the activity and subsequent rinsing, while tracing curves of isoactivity by means of a portable collimated apparatus.

Ventilation and Meteorology

In Australia, short-lived isotopes are used (1) to trace air movements in clouds, (2) to study large-scale ventilation and air pollution, (3) to detect leaks in gas distribution systems, and (4) to trace silt, effluent, and water movement, as reported by Watt.[67] Cloud-seeding experiments to increase rainfall require some knowledge of movement and dispersion of the seeding substance after release, particularly how much reaches the subfreezing temperature levels where it may act as an ice nucleating agent, leading to the formation of large ice crystals and, subsequently, rain. Copper-64 in the form of finely divided CuO is released from an aircraft during flight by using electric detonators to smash an ampule trailing behind the aircraft, and the gamma rays emitted by the material are detected by a large-crystal spectrometer as the aircraft makes a series of parallel passes

for 30 to 50 min in the vicinity of the release. By incorporation of a direction-sensing device in the detection system, it is possible to determine whether the bulk of the activity is to the right or left of the aircraft, thereby permitting proper direction for the next pass. Early tests showed that the radioisotope is swept rapidly away to other altitudes from the point of release and that dispersion in clouds is much more rapid than in clear air.

The use of Ar^{41} and Kr^{85} for ventilation studies is well established,[79] but the method is not suitable for large-scale experiments because of the potential hazard of activities required. Watt[67] reports the use of $Cu^{64}O$ particles of 1 to 3 μ in diameter for large-scale ventilation experiments or large-scale tracing of air movement in the atmosphere and the same isotope, adsorbed on the particles to be traced, in atmospheric pollution studies.

Metallurgy

Metallurgical studies with short-lived isotopes have been reported by Kohn:[80]

1. The effect of rare earths (as misch metal) admixed in very small amounts of steel was evaluated by use of La^{140} tracer to allow analysis of the rare earths by simple gamma-count rate.

2. The formation of metal crystals in a copper-aluminum alloy was studied with 12.8-hr Cu^{64}, formed by irradiation of small polished test plates of the solidified alloy. The molten alloy was cooled slowly until some crystallization had taken place and then rapidly cooled (tempered) by water. Autoradiographs showed the Cu^{64} distribution in the alloy and readily permitted differentiation between the large crystals formed during slow cooling and the minuscule crystals formed during the tempering. Varying the stage of solidification at which tempering occurs permitted one to "see" how the crystals grow.

3. A study of convection currents in industrial ingots during solidification provided explanations for the phenomena which affect unfavorably the mechanical properties and the quality of ingots. Gold-198 was added to the top of an ingot, at the moment of casting but prior to solidification; analyses of sections of the cooled ingot (either by autoradiography or by counting) showed that the gold had been distributed homogeneously throughout the ingot during the solidification process. By varying the time at which the tracer was added after casting, it was shown that, in ingots weighing up to about 40 tons, these currents exist as long as 5 hr after casting and are certainly bound to affect the segregation phenomena occurring during ingot solidification.

4. The accumulation of arsenic in steels in the oxide layer on the surface of melts was demonstrated by the activation of As^{75} to give 26.5-hr As^{76} and detection of the As^{76}. In some tests the arsenic content at the surface was as much as 40 times that in the original steel melt.

Carbon Paper

Thomas et al.[81] report an interesting use of Na^{24}, Mn^{56}, and Cl^{38}, activated in carbon paper, in a study of transfer characteristics of the carbon image on data-processing cards to and from card sorters, for example. The initial transfer of part of this carbon image from numerous cards to the machines causes malfunction of the machines; furthermore, retransfer of this carbon from the machines to subsequent cards results in loss of legibility. In the test procedure used, the activated-carbon image was transferred to card stock, a test wheel was passed over the image, and the activity on the test wheel was measured with a system comprising a Geiger-Mueller tube, a monitor used as a high-voltage power supply, a precision count-rate meter, and a recorder. Carbon paper activated for 2 hr at a flux of 1×10^{13} neutrons/(cm^2)(sec) permitted evaluation of a number of different papers. For evaluation of transfer characteristics at higher sorter speeds, or for increased sensitivity of detection, specific activities can be increased by longer activation times or by addition of up to 0.5% NaCl to the ink formulation in the carbon paper.

Medicine and Biology

At the 1962 Vienna IAEA conference on short-lived isotopes, there were a few papers discussing the uses in medicine and biology. Some of these are covered briefly here to indicate several of the newer types of applications being considered.

Loos[82] mentions the use of K^{42} and Na^{24} in studies of sodium-potassium exchange, in analysis of blood circulation, and in the determination of the influence of pharmaceutical products on ion movement. Copper-64 has been used in metabolic studies, for investigating the distri-

bution of metals in the different body organs for various periods of time after injection, and for analysis of the method of fixation of copper on striated muscle tissue and its ultimate effect on drugs such as histamine and acetylcholine. Molybdenum-99 is used to study the distribution of molybdenum in plants and nodules and the effect on the fixation of molecular nitrogen.

Anbar[83] used I^{132} to determine I^{131} damage to the thyroid. Iodine-131 is used routinely as a tracer to study the formation of protein-bound iodine (PBI) in the thyroid, and it was not known whether or not this formation was actually being affected as a result of radiation damage from the I^{131} itself. Since varying the amounts of I^{131} could at best induce only slight changes in rate of PBI formation and hence only negligible changes in total PBI, it became necessary to use I^{132} to evaluate the rate of PBI formation and its composition at any given time after the administration of I^{131}.

Rosa et al.[84] have worked out an electrolytic procedure for labeling compounds with Br^{82} in an electrolysis cell in which the anodic zone contains the substance to be labeled [e.g., insulin, fibrinogen, or human serum albumin (SA)] and is separated from the cathodic zone by a dialysis membrane. With 10 ml of $10^{-2}M$ Br^{82}-labeled NH_4Br in the anodic compartment as the source of bromine, 100 mg of dissolved SA, for example, can be satisfactorily brominated by electrolysis for about 3 hr at 0.8 volt and a current of 300 μa. Under these conditions, $\sim 2.6 \times 10^{-2}$ mg of bromine per milligram of SA is discharged, and $\sim 0.1 \times 10^{-2}$ mg of bromine is fixed in each milligram of SA. With increasing current, increasing amounts of bromine are attached; but, if the current is too high (>1.8 to 2.0 ma), the protein is denatured; if the electrolysis takes place too long, the protein is oxidized by the excess bromine. At 1.5 ma for 3 hr, $\sim 13.42 \times 10^{-2}$ mg of bromine per milligram of SA is discharged, with $\sim 1.7 \times 10^{-2}$ mg being fixed to each milligram of SA.

The interstitial use of Y^{90} needles has been described by Pierquin et al.[85] and Duggan et al.[86] The former irradiated Y_2O_3 seeds (5.0×0.6 mm) for a week at $\sim 3 \times 10^{12}$ neutrons/(cm^2)(sec), placing several of these in each needle to give an activity of 1 to 1.5 mc per centimeter of needle. The needles were used successfully in benign vascular tumors in such a way that, by creating sclerotic areas immediately around the needles (separated from each other by areas of tissue receiving little or no irradiation), an adequate sclerogenous effect would result in a certain number of tuberous angiomas while giving the patient only a weak integral dose. This protection of healthy tissue is of particular advantage with angiomas situated close to radiosensitive tissues such as eyeballs or breasts, or to the genital glands.

Duggan's group investigated the use of Y^{90} needle implants to effect pituitary ablation in the treatment of breast and prostatic cancer, diabetic retinopathy, Cushing's disease, acromegaly, and exophthalmos in Graves' disease. They found that for complete ablation two needles are advantageous and also that 100 to 200 krad is required for necrosis and ablation of the pituitary gland.

Stang[87] has suggested the use of 6-hr Tc^{99m} for tagging plasma to be used in cardiac-output and cardiac-circulation studies. As the thiocyanate, it also should be suitable for liver scanning, and Tc^{99m} can be used directly for thyroid scanning and for determining cerebral circulation times. BNL[88] has recently developed, and is now supplying, colloidal Tc^{99m}, which, when injected intravenously, produces very satisfactory scintillation scans of the human liver.

Maxfield,[89] at another conference, reviewed (37 references) some of the earlier, as well as more recent, medical applications of several short-lived isotopes. A few of these are:

1. Sodium-24: (*a*) Sodium metabolism, through the determination of total exchangeable sodium in both normal and abnormal conditions. This value represents not only serum sodium but also the exchangeable sodium content of the extracellular fluid, intracellular space, and bone; hence it is a better estimate of total body sodium than is the usual measurement of serum sodium. (*b*) Circulation studies involving, for example, determination of the vascular supply to the leg of a patient with arteriosclerosis or circulation in a pedicle skin graft. (*c*) Therapeutic treatment of bladder tumors.

2. Potassium-42: Total exchangeable potassium in the body. In this case, as with sodium, serum potassium values alone are a poor measure of changes in the total potassium content since the potassium is primarily intracellular.

3. Copper-64: This positron-emitting isotope has been used successfully in brain-tumor localization through the positron-scanning technique. It has the advantages over As^{74} of low

morbidity, no mortality, and lower radiation dose.

4. Iodine-132: Substituted for I^{131} in thyroid uptake studies. The Te^{132} cow is an advantage.

5. Iodine-128: A 25-min half-life limits the use principally to thyroid clearance studies.

6. Manganese-56: Shows some promise for liver scanning to locate primary liver tumors, liver abscesses, and areas of metastasis to the liver. It is also potentially useful for reducing radiation dose, by replacing Au^{198} in liver blood flow studies, and for studying manganese metabolism.

7. Oxygen-15: Although O^{15} has a half-life of only 2.1 min, it has been used successfully in pulmonary function studies.

8. Magnesium-28: A tracer for magnesium pools in the body.

References

1. W. F. Libby, Radioisotopes, *Nucleonics*, 15(9): 118-121 (September 1957).
2. *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. II, pp. 3-146, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
3. Neutron Activation Analysis, *Isotopes and Radiation Technol.*, 1(1): 64-77 (Fall 1963).
4. See Ref. 89, p. 59.
5. F. Nelson and K. A. Kraus, Some Techniques for Isolating and Using Short-Lived Radioisotopes, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 191-213, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.

Reactor Production

6. Oak Ridge National Laboratory, *Catalog (of) Radio and Stable Isotopes*, USAEC Report TID-18870 (4th Rev.), April 1963.
7. Catalog: *Processed Isotopes Available from Brookhaven National Laboratory*, 1960.
8. Stable Isotopes, *Isotopes and Radiation Technol.*, 1(1): 43-52 (Fall 1963).
9. C. Taylor, Comment on "Production of Short-Lived Radioisotopes," in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, p. 47, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
10. See Ref. 8, p. 50.
11. A. J. Weiss and Manny Hillman, Production of Mg^{28} — State of the Art, USAEC Report BNL-6607, Brookhaven National Laboratory, 1962.
12. L. G. Stang, Jr., A Review of the Production of "Special" Radioisotopes, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 3-29, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
13. I. Dostrovsky and Z. Fraenkel, Calculated Formation Cross Sections of Ca^{45} and Ca^{47}, *J. Inorg. Nucl. Chem.*, 21: 10-14 (1961); same as IAEA Report RI/11.
14. A. Ward, Comment on "The Scottish Research Reactor Centre," in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, p. 122, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
15. J. L. Sommerville (Ed.), *The Isotope Index*, 7th ed., Scientific Equipment Company, Indianapolis, 1963–1964.
16. Catalog: *Processed Isotopes and Sealed Sources*, C.E.A. Dept. des Radioelements, Gif-sur-Yvette, France, August 1962.
17. Catalog: *Radio-Isotopes*, Institutt for Atomenergi, Kjeller, Norway, June 1963.
18. Catalog: *Isotopes*, 2d ed., Moscow, 1962.
19. K. Heydorn, Experiences with the Irradiation of Ammonium Bromide, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 123-139, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
20. W. W. Meinke, Techniques for Fast Radiochemistry, in M. W. Brown (Ed.), *Modern Trends in Activation Analysis*, pp. 36-40, A & M College of Texas, College Station, Tex., 1962.
21. W. W. Meinke, A. Ghiorso, and G. T. Seaborg, Artificial Chains Collateral to the Heavy Radioactive Families, *Phys. Rev.*, 81: 782-798 (especially pp. 795-798) (1951).
22. Y. Kusaka and W. W. Meinke, Rapid Radiochemical Separations, USAEC Report NAS-NS-3104, National Academy of Sciences–National Research Council, December 1961.
23. P. C. Aebersold and A. F. Rupp, Production of Short-Lived Radioisotopes, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 31-47, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
24. A. F. Rupp, Production of Radioisotopes with Very High Specific Radioactivity, in *Proceedings of the Fifth Japan Conference on Radioisotopes, Tokyo, May* 21–23, 1963, pp. 2-22 to 2-29.
25. G. Friedlander and J. W. Kennedy, *Nuclear and*

Radiochemistry, p. 332, John Wiley & Sons, Inc., New York, 1955.

26. E. R. King, W. S. Maxfield, R. Sharp, and R. Druyan, Production of Short-Half-Life Radioisotopes, *Radiology*, 71: 862 (1958).
27. L. G. Stang, Jr., W. D. Tucker, R. F. Doering, A. J. Weiss, M. W. Greene, and H. O. Banks, Jr., Development of Methods for the Production of Certain Short-Lived Radioisotopes, in *Radioisotopes in Scientific Research*, Vol. I, pp. 50-68, Proceedings of the First UNESCO International Conference, Paris, 1957, Pergamon Press, New York, 1958.
28. R. Stiennon-Bovy and G. Haegeman-Geladi, Study of the Preparation of Tellurium-132 and Iodine-132, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 141-157, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963; also in USAEC Translation AEC-tr-5793.
29. M. Barrachina Gomez, Production of Iodine-132 from Irradiated Uranium Tetrafluoride, *ibid.*, pp. 159-169; also in USAEC Translation AEC-tr-5752.
30. L. G. Stang, Jr., and P. Richards, Tailoring the Isotope to the Need, *Nucleonics*, 22(1): 46-49 (January 1964).
31. Margaret W. Greene, R. F. Doering, and M. Hillman, Milking Systems: Status of the Art, *Isotopes and Radiation Technol.*, 1(2): 152-154 (Winter 1963–1964); same as USAEC Report BNL-6697.
32. K. Frühauf, Studies with Short-Lived Radioisotopes in the Chemical Process Industry, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 249-257 (especially pp. 254-255), proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
33. C. Taylor, R. West, and M. Whiting, The Production and Distribution of Short-Lived Radioisotopes in the United Kingdom, *ibid.*, pp. 67-82.
34. W. W. Meinke, Handling and Separation of Short-Lived Radioisotopes from Research Reactors, *ibid.*, pp. 93-104.
35. W. W. Meinke, Pneumatic Tubes Speed Activation Analysis, *Nucleonics*, 17(9): 86-89 (1959).
36. A. E. Greendale and D. L. Love, A System for Rapid Handling of an Irradiated Solution, *Nucl. Instr. Methods*, 23: 309-312 (1963).
37. D. N. Sunderman and W. W. Meinke, Evaluation of Radiochemical Procedures, *Anal. Chem.*, 29: 1578-1589 (1957).
38. D. N. Sunderman, I. B. Ackermann, and W. W. Meinke, Radiochemical Separation of Indium, *Anal. Chem.*, 31: 40-44 (1959).
39. C. W. Townley, T. S. Elleman, and D. N. Sunderman, Radiochemical Separation Techniques for Short-Lived Fission Products, *Trans. Am. Nucl. Soc.*, 5: 194 (1962).
40. J. R. DeVoe and W. W. Meinke, Radiochemical Separations of Cadmium, *Anal. Chem.*, 31: 1428-1432 (1959).
41. W. W. Meinke, Nuclear Chemical Research: Radiochemical Separations and Activation Analysis, Progress Report 7, November 1957–October 1958, USAEC Report AECU-3887, University of Michigan, Nov. 1, 1958.
42. U. Schindewolf and M. Wahlgren, The Rhodium, Silver, and Indium Content of Some Chondritic Meteorites, *Geochim. Cosmochim. Acta*, 18: 36-41 (1960).
43. D. G. Kaiser and W. W. Meinke, Activation Analysis of Trace Cobalt in Tissue Using 10.5-Minute $^{60-m}$Co, *Talanta*, 3: 255-260 (1959–1960).
44. O. Høgdahl, in Activation Analysis, Nuclear Chemical Research: Radiochemical Separations, Progress Report 11, November 1961–October 1962, R. S. Maddock and W. W. Meinke (Eds.), USAEC Report TID-17272, University of Michigan, Nov. 1, 1962.
45. E. L. Steele and W. W. Meinke, Determination of Rhodium by Thermal Neutron Activation Analysis Using γ-Ray Spectrometry, *Anal. Chim. Acta*, 26: 269-274 (1962).
46. R. Kuroda, Activation Analysis, Nuclear Chemical Research: Radiochemical Separations, Progress Report 11, November 1961–October 1962, R. S. Maddock and W. W. Meinke (Eds.), USAEC Report TID-17272, University of Michigan, Nov. 1, 1962.
47. C. K. Kim and W. W. Meinke, Thermal Neutron Activation Analysis of Titanium Using 5.8-Minute Titanium-51 and Rapid Radiochemical Separations, *Talanta*, 10: 83-89 (1963).
48. W. W. Meinke, Activation Analysis Utilizing Fast Radiochemical Separations and Portable Neutron Generators, in *Radioisotopes in the Physical Sciences and Industry*, Report STI/PUB/20, Vol. II, pp. 277-290, proceedings of a conference held in Copenhagen, September 6–17, 1960, International Atomic Energy Agency, January 1962.
49. K. Rengan and W. W. Meinke, Rapid Radiochemical Separation and Activation Analysis of Rare Earth Elements, *Anal. Chem.*, 36: 157-161 (1964).
50. R. Loos, Production and Utilization of the Isotopes Sodium-24, Potassium-42, Copper-64, and Molybdenum-99, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 215-220, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963; also in USAEC Translation AEC-tr-5749.
51. F. W. Felix, D. Pirrwitz, and E. Szabó de Bucs, Production of Short-Lived Radionuclides at the Hahn-Meitner Institute in West Berlin, *ibid.*, pp. 105-112.

52. C. K. Kim, Short-Lived Radioisotope Production, Processing, Distribution, and Applications in Korea, *ibid.*, pp. 221-226.

Applications

53. L.-G. Erwall, H. G. Forsberg, and K. Ljunggren, Short-Lived Isotopes Used as Tracers in Industry (with special reference to Swedish industry), *ibid.*, pp. 229-247.

54. J.-P. Adloff and M. Adloff-Bacher, Application of the β-Decay of Te^{132} for the Preparation of I^{132}-Labeled Molecules, *ibid.*, pp. 181-189; also in USAEC Translation AEC-tr-5758.

55. K. A. Kraus, H. O. Phillips, and F. Nelson, Some Applications of Radioisotopes in Physical Chemistry—Two-Phase Equilibria and Packed-Column Techniques, in *Radioisotopes in the Physical Sciences and Industry*, Report STI/PUB/20, Vol. III, pp. 387-406, proceedings of a conference held in Copenhagen, September 6–17, 1960, International Atomic Energy Agency, Vienna, March 1962.

56. K. A. Kraus and F. Nelson, Anion Exchange Studies of Metal Complexes, in *The Structure of Electrolyte Solutions*, W. J. Hamer (Ed.), pp. 340-364, John Wiley & Sons, Inc., New York, 1959.

57. O. Hahn and O. Müller, A New Method for Studying the Surface and Surface Changes of Finely Divided Precipitate, *Z. Elektrochem.*, 29: 189-192 (1923).

58. J. H. Wang, in *Radioactivity Applied to Chemistry*, A. C. Wahl and N. Bonner (Eds.), p. 62, John Wiley & Sons, Inc., New York, 1951.

59. See Ref. 55, p. 204.

60. J. du Domaine, R. L. Swain, and O. A. Hougen, Cation Exchange Water-Softening Rates, *Ind. Eng. Chem.*, 35: 546-553 (1943).

61. G. E. Boyd, A. W. Adamson, and L. S. Myers, The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. Kinetics, *J. Am. Chem. Soc.*, 69: 2836-2848 (1947).

62. F. T. Wall, P. F. Grieger, and C. W. Childers, A Rapid Method for Measuring Diffusion Coefficients for Solutions, *J. Am. Chem. Soc.*, 74: 3562-3567 (1952).

63. K. Frühauf, Studies with Short-Lived Radioisotopes in the Chemical Process Industry, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 249-257, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.

64. I. Bjerle, Studies of Powder Mixing with Short-Lived Radioisotopes, *ibid.*, pp. 259-268.

65. H. G. Forsberg and I. Bjerle, Control of Powder Mixing with Radioactive Isotopes, *Tek. Tidskr.*, 92: 717-720 (1962).

66. B. R. Petersen, Radioactive Surface Labelling of Powdered Materials by Means of Gold-198, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 269-274, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.

67. J. S. Watt, Some Recent Applications of Short Half-Life Radioisotopes in Australia, *ibid.*, pp. 343-355.

68. C. Tellier, G. Courtois, and M. Gasnier, Some Applications of Short-Lived Radioisotopes in the French Gas Industry, *ibid.*, pp. 357-382; also in USAEC Translation AEC-tr-5899.

69. C. Maille, J. Moinard, D. Blanc, and J. Fontan, Measurement of the Specific Gravity of the Water-Steam Emulsion Flowing in a Screen Tube of an Industrial Boiler Using Sodium-24, *ibid.*, pp. 415-432; also in USAEC Translation AEC-tr-5772.

70. P. A. Lottes and W. S. Flinn, A Method of Analysis of Natural Circulation Boiling Systems, *Nucl. Sci. Eng.*, 1: 461-476 (1956).

71. W. H. Cook, Boiling Density in Vertical Rectangular Multichannel Sections with Natural Circulation, USAEC Report ANL-5621, Argonne National Laboratory, November 1956.

72. K. Akerman, M. Brafman, H. Fik, J. Kitala, M. Nowak, and A. Poczynajło, Separation of Impurities in the Zinc Rectification Process by Radioactive Isotopes, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 305-318, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.

73. J. N. Gregory, Some Recent Developments in the Applications of Radioisotope Techniques in Australia, in *Radioisotopes in the Physical Sciences and Industry*, Report STI/PUB/20, Vol. I, pp. 415-431, proceedings of a conference held in Copenhagen, September 6–17, 1960, International Atomic Energy Agency, Vienna, January 1962.

74. O. Berg and E. Somer, Determination of the Distribution of Sewage Concentration in Large Natural Waters from Planned Sewage Outlets, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 405-414, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.

75. E. I. Goodman, A Radiotracer for Studying Sewage Distribution, *Ind. Eng. Chem.*, 50: 210-211 (1958).

76. K. Ljunggren, L.-G. Erwall, J. Rennerfelt, and T. Westermark, Tracing of Water Flow by Means of Radioactive Isotopes and Scintillation Counters, *Intern. J. Appl. Radiation Isotopes*, 5: 204-212 (1959).

77. E. Gaspar, M. Oncescu, P. Sandru, L. Grigorescu, M. Birnbaum, and T. Teitel, Use of Na^{24} as Tracer in Public Works and Hydrology, in

Production and Use of Short-Lived Radioisotopes from Reactors, Report STI/PUB/64, Vol. I, pp. 393-403, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963; also in USAEC Translation AEC-tr-5751.

78. J. Guizerix and R. Cornuet, Applications of Sodium-24 to Flow-Rate Measurements and Leak Detection, *ibid.*, pp. 383-392; also in USAEC Translation AEC-tr-5750.
79. B. G. Collins and D. B. Smith, The Measurement of Ventilation Rates Using a Radioactive Tracer, *J. Insl. Heating Ventilating Engrs.*, 23: 270 (1955).
80. A. Kohn, Some Applications of Short-Lived Radioisotopes in the Study of Metals, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. I, pp. 285-304, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963; also in USAEC Translation AEC-tr-5824.
81. C. C. Thomas, Jr., R. F. Horan, and D. M. Hart, Test Method for Determination of Carbon Paper Transfer Characteristics, *ibid.*, pp. 275-284.
82. See Ref. 50, p. 219.
83. M. Anbar, Applications of Iodine-132 in Studies of Thyroxine Turnover, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Report STI/PUB/64, Vol. II, pp. 147-159, proceedings of a seminar held in Vienna, November 5–9, 1962, International Atomic Energy Agency, Vienna, March 1963.
84. U. Rosa, G. A. Scassellati, and G. Pennisi, Bromine-82 Labeling of Human Serum Albumin, Insulin, and Fibrinogen by Electrochemical Means, *ibid.*, pp. 161-174.
85. B. Pierquin, M. Mortreuil, H. Beyer, J. Dutreix, D. Chassagne, P. Galle, and R. Jammes, Yttrium-90 Needles in Interstitial Beta-Ray Therapy, *ibid.*, pp. 201-212; also in USAEC Translation AEC-tr-5825.
86. Mary H. Duggan, Elizabeth Jones, J. R. Mallard, and G. F. Joplin, The Technique and Dosimetry of Pituitary Implantation Using Sources of Y^{90}, *ibid.*, pp. 213-223.
87. L. G. Stang, Jr., Supplementary Discussion, *ibid.*, p. 223.
88. Brookhaven National Laboratory, Third Progress Report, Nuclear Engineering Department, September–December 1963, USAEC Report BNL-841.
89. W. S. Maxfield, Medical Applications of Short Half-Life Isotopes, in *Proceedings of the Second Annual Texas Conference on the Utilization of Atomic Energy, A & M College of Texas, College Station, November* 12–13, 1959, Texas Engineering Experiment Station Misc. Publ. E-72-60, pp. 57-61, 1960.

Section

II

Isotopes and Radiation Technology

Isotope Technology Development

The applications of isotope technology to industry and to research may be conveniently divided into the following broad fields: neutron activation analysis, radiometric analysis, tracer uses, isotope measurement and control systems, radiation absorptiometry, nondestructive testing by radiography, and ionization technology. In this issue of *Isotopes and Radiation Technology*, tracer uses of isotopes in industry and research are featured, whereas in earlier issues radiometric analysis,[1] neutron activation analysis,[2] and isotope measurement and control systems[3] were reviewed.

Following a brief historical background, several new uses of isotopes as tracers that have been developed under contract with the AEC Division of Isotopes Development are described, e.g., a new instrument for determination of flow of ocean currents, a new and better method for the introduction of tritium into organic compounds, and an engineering study of water flow using a stable isotope. This is followed by a discussion of uses of isotopes in the canning industry, a review of the literature describing the use of isotopes in wear and lubrication testing, a survey of some uses of isotopes in the foreign coal industry, and a summary of some instrument development work to provide better techniques for the detection of tracers done under contract with the Division of Isotopes Development.

The use of radioisotopes as tracers was developed with naturally radioactive isotopes; however, until the discovery of artificial radioactivity, these techniques were no more than laboratory curiosities. After reactor-produced isotopes became available in 1946, tracer techniques rapidly moved out of the laboratory and into use in industrial processes and other large-scale engineering applications.

In 1913 Hevesy and Paneth used radium-D as a tracer for lead in the determination of the solubility of lead sulfide and lead chromate in water.[4] They followed this original study with many more in which the naturally radioactive isotopes of lead and bismuth were used as tracers.[5]

In 1923 Hevesy first used an isotope of lead (thorium-B) to study its distribution in the horsebean *(Vicia faba)*.[6] The following year, in cooperation with a dermatologist who was interested in bismuth salts for the treatment of syphilis, he studied the distribution of bismuth (radium-E) in the rabbit.[7] In 1934, after the discovery of deuterium by Urey, Hevesy received some heavy water from him and used it to measure the mean lifetime of water in the human body[8] and the speed of exchange of water between the body of a goldfish and its environment.[9] To complete the picture, in 1935, shortly after the discovery of artificially radioactive isotopes, Hevesy used P^{32} to study the metabolism of phosphorus in rats and humans. In his early work,[10,11] he made P^{32} by bombardment of sulfur with neutrons from a radium-beryllium source, but in later work[12] he used a higher specific-activity P^{32} made by Lawrence in the University of California cyclotron.

An early industrial use was by Ferris,[13] who received a patent in 1943 on a process for determining the wear of surfaces of bearings, pistons, or cylinders by incorporating P^{32} into steel. This research was done at Battelle Memorial Institute with P^{32} prepared in the Ohio State University cyclotron. Clark, Gallo, and Lincoln[14] in 1943 studied the effect of sulfur additives on oil-film adhesion. They prepared the additives by the addition of S^{35}, made in the cyclotron by the $Cl(n,p)S^{35}$ reaction, to olefins. The amount of oil adhering to metal and glass surfaces was determined by counting. In 1944 Sakmann, Burwell, and Irvine[15] used Cu^{64} tracer to determine the amount of metal transferred from on part to another as a result of friction.

The Cu^{64} was made *in situ* by bombarding beryllium-copper alloys with deuterons in the cyclotron.

Following these early developments, isotopic tracers have been used in many typical industrial and engineering applications such as:

- —to test lubricating qualities of oils and greases[14]
- —to study the effect of friction on engine parts[13,15,16]
- —to determine the wear resistance of tools and dies[17–19]
- —to measure flow rate of liquids or gases[20–24]
- —to study flow patterns of liquids, gases, or solids in industrial processes[25]
- —to detect leaks in pipes, conduits, and process equipment[24,26–29]
- —to test the efficiency of mixing equipment[25,30]
- —to determine reaction mechanisms[31,32]
- —to trace air movements[33–36]
- —to study the movement of surface and underground water[37,38]
- —to study the movement of sand on beaches and underwater[39,40]
- —to study the separation of materials by fractionation, washing, or other processes[41–45]

The most widespread and successful uses of radioactive tracers in industrial research have been in the first three applications mentioned above. An extensive literature review on this subject, taken from a recent report,[16] is given on page 256. *Radioisotope Applications Engineering*[46] also gives a good discussion of this subject.

Several of the other applications in the above list come under the broad heading of hydrology. This subject was reviewed extensively at a symposium[47,48] sponsored by the International Atomic Energy Agency (IAEA) in Tokyo in March 1963, where 27 papers were presented from 11 different countries. The use of radioisotopes to make river and groundwater flow measurements and to trace groundwater, sand, and beach movement were among the subjects discussed.

The petroleum industry has been one of the most extensive users of radioisotope tracers.[49] King,[50] in a review of the uses of isotopes in refinery operations, said:

> Radioisotopes are important tools in the progressive operator's kit. Future generations will wonder how a refinery was ever run economically without them. Uses are increasing more than exponentially, and oil companies measure savings in millions of dollars per year.

Because research engineers and scientists in the petroleum industry have been aware of the advantages offered by isotopes in industrial use, illustrations of almost every type of tracer use of isotopes can be found in publications from this industry (Table II-1).

Table II-1 USES OF ISOTOPES AS TRACERS IN THE PETROLEUM INDUSTRY*

Process	Isotopes used	References
Liquid (and fluidized solid) flow rates	Sc^{46}, Ce^{144}, I^{131}, I^{132}, Rb^{86}, Br^{82}	20–22, 49–51
Catalyst behavior: mixing, inventory, and stack losses	Ba^{140}, Ce^{144}, Sc^{46}, Cr^{51}, Rb^{86}, Co^{60}, Au^{198}	31, 32, 44, 45, 51, 54–56
Gas flow rates	H^3, Br^{82}, Kr^{85}	20, 49, 57
Leak testing	Sb^{124}, Na^{24}, Br^{82}, Kr^{85}, Cs^{134}	50, 58, 59
Entrainment	Ba^{140}, C^{14}, Sb^{124}, Co^{60}	31
Mixing	I^{132}	25, 30, 51–54
Studies of reaction mechanism	C^{14}	31, 32

*Modified from Ref. 50.

These studies have resulted in several patents. Metcalf[60] and Hull[61] have received patents for methods using various isotopes to measure flow in pipes, and Mitchell and Kinsella[62] for a method to determine catalyst flow with Co^{60} as a tracer.

Specific Tracer and Radiochemical Applications

Much work is now being done to develop industrial and other engineering uses of isotopes as tracers. In this issue a progress report is given on the development of a deep-water current analyzer; this is followed by a description of a new method for labeling organic compounds with tritium and a study using stable manganese as a tracer and activation analysis for the determination.

Ultrasensitive Analyzer for Measuring Speed of Water Currents

Workers at the William H. Johnston Laboratories under contract with the AEC Division

of Isotopes Development have developed a sensitive instrument for measuring the speed and direction of very slow water currents.[63–65] With less than 1 μc of I^{131} activity per test, this Deep Water Isotopic Current Analyzer (DWICA) can measure currents as low as 0.01 knot, which is a significantly greater sensitivity than previous instruments had. The upper measurable limit is 1 knot, but, with suitable design modifications, this could easily be raised to 5 knots. No data have been given on the precision or accuracy of the instrument. The instrument can also indicate both horizontal and vertical directions of current flow, although in tests to date no vertical component has been detected.

An earlier instrument of this design performed well in tests but required operator attention. An improved instrument has been modified electronically to operate for long periods without attention. In the discussion below, the original instrument is described,[63,64] followed by a summary of changes that were made to achieve more automatic operation;[65] finally some test data obtained with the instrument are presented.[63,65]

DWICA: Principle of Operation. The principle of operation of the DWICA is simple, although the instrumentation for the measurements is complex. Let us envision a planar ring of 16 counters oriented so that the direction of water flow is in the same plane as the counters (Fig. II-1). The ring of counters is not completely closed, the spaces between them allowing water to flow through the ring with little interference. If a small quantity of radioactive solution is injected at the center of the ring, the time between injection and detection of the activity depends on the speed of the current and the radius of the ring. A calibration curve showing the relation between current speed outside and inside the ring was established empirically at the National Bureau of Standards (NBS). Thus current speed is easily calculated from the elapsed time, the radius of the ring of counters, and the calibration curve.

The particular counter that is downstream from the center at the time of measurement observes the activity, and the current direction is obtained from a knowledge of which counter was downstream and the orientation of the ring of counters with respect to north.

In practice, 1.0 ml of solution containing I^{131} is injected in a fraction of a second. Laboratory studies have shown that diffusion of the injected material is not a problem in the speed ranges of interest (0.1 to 10 cm/sec). Thus the injected radioactivity may be considered a point source. As the activity approaches a counter, the counting rate increases to a maximum as the activity passes the counter and decreases to background as the activity leaves. The elapsed time then is the time from injection to the observation of the maximum counting rate.

DWICA I. For simplicity, the description of the instrument is given in three parts: (1) the underwater unit; (2) the electronics, which for the most part are located on shipboard; and (3) the recording system, also located on shipboard.

Underwater Unit. The DWICA I unit, shown in Fig. II-2, was constructed to provide the least interference with current flow. The detectors were 16 scintillation counters, eight of which

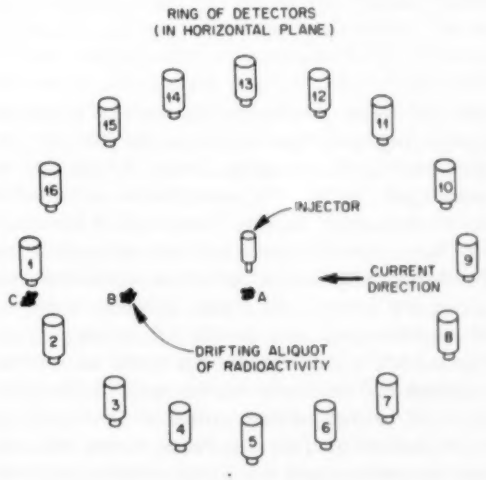


Fig. II-1 Schematic diagram of the operation of DWICA.

Automatic Sequence of Operations

1. Tracer quantity of radioactive solution injected at *A*.
2. Radioactivity (*B*) drifts toward a detector.
3. Detection of radioactivity at *C* indicates and records automatically the time-of-drift. Current velocity is distance divided by time-of-drift.
4. As shown, counter 1 receives activity, and the counter that is activated is recorded, thus giving direction of current.
5. This measurement is automatically repeated at programmed intervals.

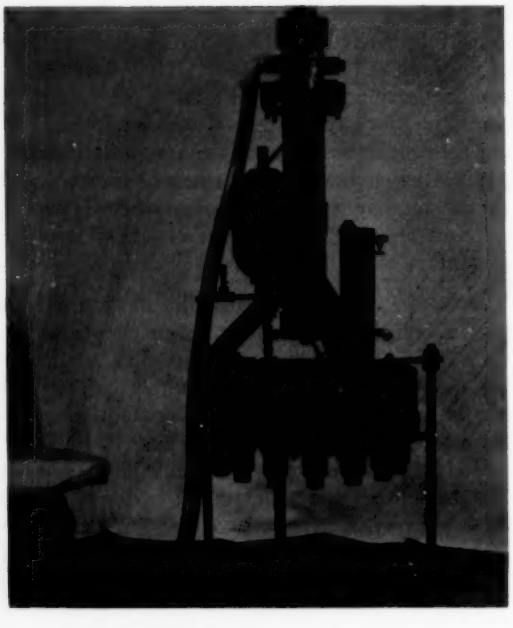


Fig. II-2 DWICA I.

can be seen protruding downward from the metal ring near the center of the picture. The counters were arranged so that the axes of the phototubes lay on a right-circular cylinder 20 in. in diameter, and the ring support structure for the counters contained the preamplifiers. The large cable on the left of the apparatus contained the power and signal conductors for the 16 counters as well as the 16 preamplifiers. The air hose, entering the top of the main stem, supplied air pressure to the body of the apparatus to prevent water pressure from pushing the counters up into the support ring when the unit was submerged and to keep water out of the ring. The unit was mounted on a stand, which was fastened to a large plate when the instrument was used in the ocean. The radioactive solution was stored under pressure in the bulbous tank fastened to the left of the main stem of the apparatus and was injected into the center of the counters on command from the surface by opening a small solenoid-operated valve. The injector is not visible in Fig. II-1.

The DWICA could be located in a spot where the water current was not moving in a horizontal plane. In this case, radioactive solution injected into the plane of counters would be carried up or down, away from the detectors. Under these conditions, a much smaller than usual response, or in extreme cases no response, would be obtained. This problem was solved by raising or lowering the point of injection with respect to the counters until the count rate was a maximum. Under these conditions, DWICA gives the speed and direction of the current and indicates the amount of vertical movement relative to horizontal movement. The point of injection was moved with a hydraulic system, the master cylinder being on the surface and the slave cylinder on the underwater unit. The slave cylinder and its support are shown extending above the ring and located on the right of the main stem of the apparatus in Fig. II-2.

Electronic Units. With the exception of the preamplifiers, which were in the underwater unit, the electronic equipment for control and for interpretation of data was located on shipboard. This basic unit, which interpreted the signals from the counters, was a transistorized diode computer logic circuit. This circuit gave both the elapsed time between injection and detection of the radioactive solution and indicated direction by showing which counter was experiencing the highest counting rate. Each of the 16 scintillation detectors was connected with a linear amplifier, a discriminator, and a count-rate circuit.

The counting rates from these 16 circuits were indicated on the control panel by a circle of 16 indicator lights and a single counting-rate meter. The circle of lights on the control panel indicates direction in the following way: At any time, one of the 16 counters is observing a counting rate higher than any other owing to statistical random fluctuation in radioactivity background. When a measurement is not being made, the 16 lights flash on and off in random sequence. However, in the course of the measurement, the injected radioactivity passes one of the 16 counters, and, during the passage of the radioactivity, this counter continually observes the highest counting rate, and only the light corresponding to it is lighted. The count-rate meter on the panel indicates the sum of the counting rates of the 16 counters and gives a maximum reading as the injected radioactivity passes a counter.

Switches on the panel permitted selection of different lengths of time, during which the solenoid-operated injection valve for I^{131} remained open. The valve could be opened for 40, 80, 120, 330, 680, or 820 msec. A register re-

corded the number of injections, and the injection system could be actuated manually or automatically.

A timer-programmer was installed in parallel with the existing manual switch on the basic unit to make the overall system automatic. With this programmer the DWICA could be operated at preset intervals, from 30 sec to 120 min. Measurement of current speed and direction was thus completely automatic since the programmer started the measurement at the preset time by injecting radioactive solution and starting the recording system. The interpretation computer then indicated both the current flow direction and the current speed by giving the time elapsed between injection and detection. This information was recorded on the strip chart, and the programmer reset itself for the next measurement at the end of the off-time.

Recording System. A permanent record of each measurement of current velocity was obtained with a dual-pen strip-chart recorder. One pen recorded the activity observed with the count-rate meter, i.e., the sum of the counting rates of all 16 detectors. At the start of a measurement, the injection was marked on the strip chart by a dip of the count-rate meter toward zero. The direction of the current was obtained with the other pen, which was arranged to record on a separate line for each counter. Counter 1 was represented by full deflection of the pen, and counter 16, by minimum deflection; the other counters were spaced in order in between.

Figure II-3 shows a measurement made in December 1961 in the Severn River. The lower chart is a record of counting rate vs. time. Prior to the injection, the chart was stopped to save paper and to make data handling easier, and thus the vertical mark at that time shows that the background had fluctuated. At the far right of this section of the chart, there is a rapid dip of the pen, indicating that the injection was made at this time. The chart was started at the time of the injection, and the counting rate increased as the activity approached a counter, reached a maximum after several divisions, and then returned to background. Since the chart speed was known, the time between injection and maximum counting rate was easily determined.

The upper chart is a plot of counter number vs. time. Before the chart was started, the pen oscillated, indicating that different counters were observing activity. The pen did not move all the way across the chart because it could not follow the rapid variation of maximum counting rate from one counter to another; thus its average position is midway between counters 8 and 10. When the chart started, the pen fluctuated until the activity neared a counter (known from previous calibration to be number 4). At this time, counter 4 was observing the maximum counting rate continuously, and the pen indicated that counter; it started fluctuating again as the activity left the vicinity of this counter and returned to its normal deflection range when the observed counting rate reached background.

DWICA II. After the successful operation of DWICA I, several new automatic control systems were added to make the programming and recording system more automatic and trouble-free: (1) the automatic digital converter system, which rapidly converts the data of time-of-drift and of recipient detector to digital printed form; (2) the electronic servo-injector control system, which automatically injects the optimum amount of radioactive solution; (3) the automatic program control system, which varies the repetition rate of radioisotope injections; and (4) the automatic logic alarm system, which indicates a malfunction in any part of the instrument. The effects of each of these systems on the overall measurements are described below; the detailed circuits may be found in Ref. 65.

These systems have made DWICA II an automatic instrument. They are, both individually and as an integrated system, capable of multipurpose application wherever kinetic conditions of fluid flow require measurement. Thus applications are possible in pipe flow studies, in chemical engineering processing, and in various areas of hydrology and limnology.

Automatic Digital Converter System. This system prints out the date and time of measurement, drift time of injected activity, and the number of the counter that observed the activity (i.e., direction). Obviously, this readout system is superior to strip-chart recording since the bulk of paper to be handled is reduced by a factor of 100 in length and of 10 in width, the drift time need no longer be calculated by measuring distances on the chart, and the direction is given directly rather than by a calibration of pen deflection vs. counter number. All that remains to be done is to calculate the apparent

drift speed from drift time, convert this to true speed by means of the calibration curve, and write down the direction in degrees from knowledge of the absolute orientation of the DWICA.

Electronic Servo-Injector Control System. The purpose of this apparatus is to adjust, when necessary, the amount of radioactivity injected at the start of current velocity measurement. If insufficient radioactivity is injected, only a very small peak counting rate will be obtained. Superimposed on the background counting rate with its fluctuations, this peak will be indistinct, making precise current velocity determination difficult or impossible and rendering current direction uncertain. If the correct amount of activity is injected, a good measurement is obtained (Fig. II-3). If too much activity is injected, the peak becomes too broad, and activity is wasted.

A manual time selector switch that may be used to underride the automatic servo-injector system is also available. This feature is par-

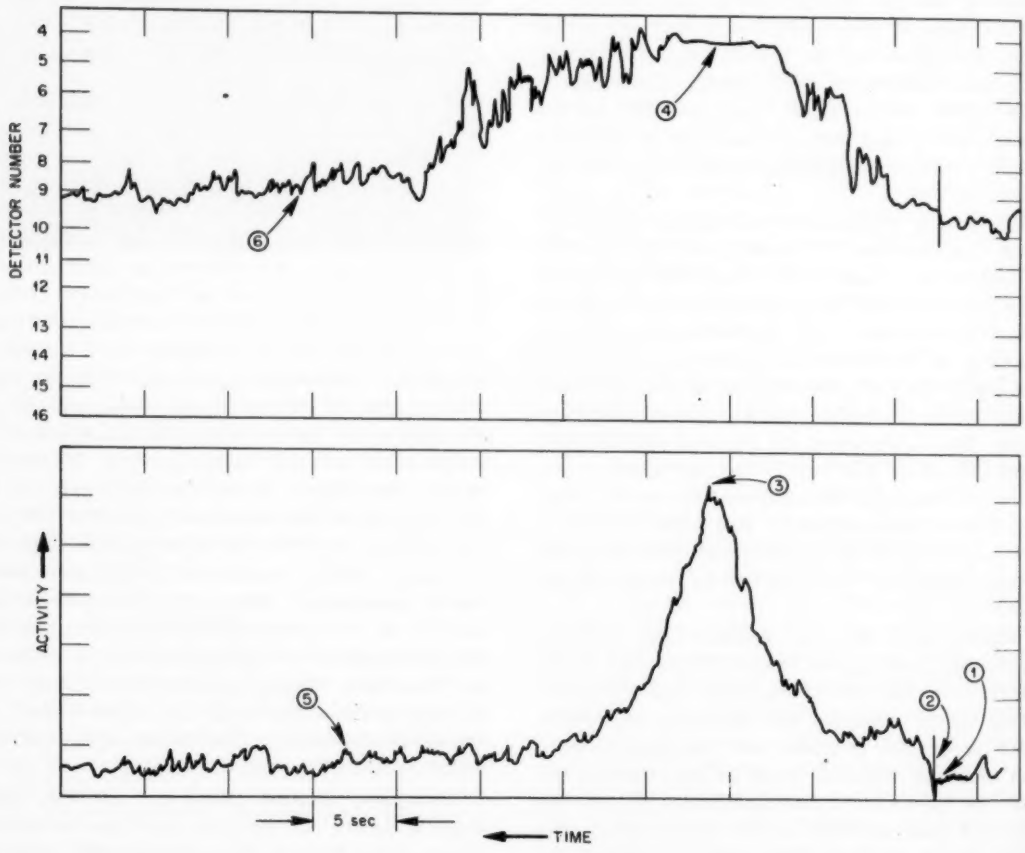


Fig. II-3 Typical recording of results from DWICA I tests in the Severn River, Round Bay, Md. Injection, 0930 hr, Dec. 20, 1961; current speed, 3.50 cm/sec; current direction, 15°T.C.

Explanation of Circled Numbers

1. Chart previously stopped after last measurement.
2. Radioactivity injected here. Dip indicates automatic injection and chart starting.
3. Activity passes counter here. Chart distance from injection shows current speed.
4. Step function at this level indicates activity at counter or current direction of 15°T.C.
5. Activity leaves DWICA, and background returns to normal.
6. Direction circuitry returns to random counter preference.

ticularly valuable in initial research measurements in combination with pen recorder or visual monitoring of the count-rate meter.

Automatic Program Control System. This element decides how often to make measurements. If current velocities are slow, e.g., less than 2 cm/sec, they need not be measured very often. As soon as a fast current measurement is obtained, the time interval between measurements should be shorter so that changes in current behavior are resolved.

Automatic Logic Alarm System. The automatic systems described above have made possible automatic operation of the instrument in field tests. In approaching these tests, it was decided that an automatic alarm system would add much to the reliability of the overall instrumentation. The logic of the alarm system is based on two questions which are automatically asked prior to each measurement: "Was the last injection detected?" and "After the last injection was detected, did the background return to normal?" In this system, a transistor-diode logic circuit requires a "yes" to both questions before allowing the next injection. If either answer is "no," a buzzer alarm is turned on, during the operation of which the instrument refuses to make injections. In the many tests to date, this system has never given an alarm except for test purposes.

Instrument Performance. DWICA I was calibrated at NBS, and then a series of field tests was made cooperatively with the Chesapeake Bay Institute of Johns Hopkins University. After the instrument was modified, further tests were made in Chesapeake Bay. The complete results[63,65] of these tests are extensive; however, a few of them are given here to show the kind of data that this instrument can supply.

Calibration. DWICA I was calibrated at the NBS Meter Testing Pool, which is 400 by 6 ft and 6 ft deep. On either side of the pool are rails on which runs a small truck for pulling the apparatus to be tested through the water at different speeds. Current speed was measured at different truck speeds, and the calibration curve of apparent, or measured, speed vs. known speed was thus established (Fig. II-4) for speeds from 0.6 to 7.6 cm/sec (0.01 to 0.15 knot). Below 1 cm/sec the apparent speed is equal to the actual, but above 1 cm/sec there is sufficient drag on the water current to decrease the speed of currents passing between the counters.

DWICA I Tests. In two series of tests on DWICA I made in December 1961 in Round Bay, Md.,[66] current speeds from 0.5 to 10 cm/sec (0.01 to slightly less than 0.2 knot) were measured.

In January 1962, in tests in the Severn River approximately opposite the Naval Academy,

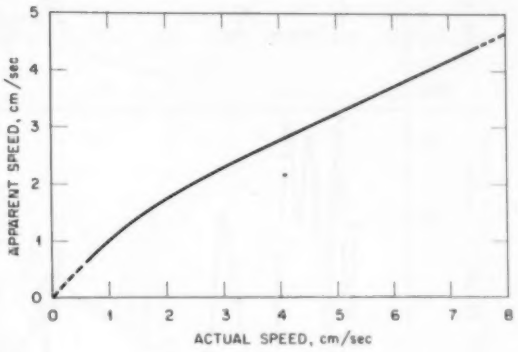


Fig. II-4 DWICA calibration curve from field tests at National Bureau of Standards.

measurements were begun just after 2 p.m. on January 23 and continued until 3 p.m. on January 26. During this 72-hr period, more than 600 measurements of current speeds from 0.5 to 17 cm/sec and directions were measured. Measurements were made at intervals ranging from 2 to 20 min, depending on whether the speed and direction appeared to be changing rapidly or remaining constant. The water at the point of measurement was 19 ft deep, and measurements were made 13 in. from the bottom.

The data, part of which are shown in Fig. II-5, were subjected to detailed theoretical analyses. The vector component, or the upstream velocity projection, was calculated for each measured point with negative values representing downstream motion. From these vector diagrams, the integral representing the net motion of water upstream was formed.

Figure II-6, where these calculated values of upstream velocity vectors are plotted for the measured points given in Fig. II-5, shows that the correlation between current and tidal movements is very good and that water flows upstream during flood and downstream during ebb tides. Interestingly, toward the end of flood or ebb tide, currents sometimes move counter to the major tidal direction.

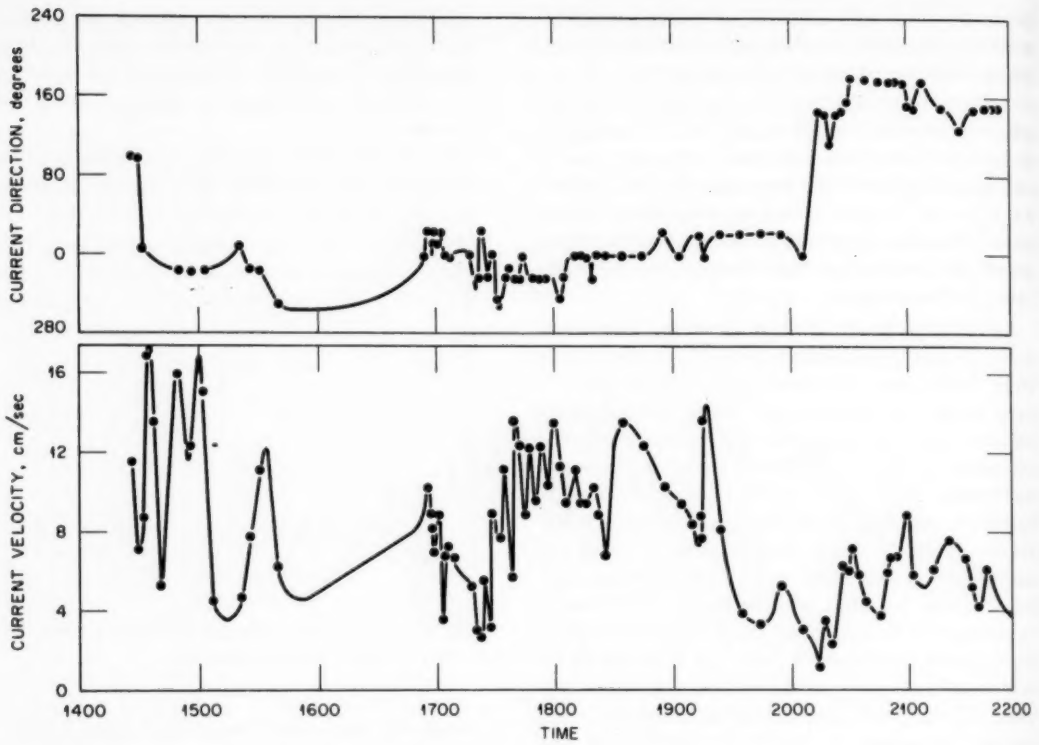


Fig. II-5 Typical current flow data taken with DWICA I at Annapolis, Md., on Jan. 23, 1962, 1400 to 2200 hr.

DWICA II Tests. After pretesting and calibrating the DWICA II, tests were made off Spriggs Pond in the Magothy Estuary using all the automatic systems. The new automatic print-out recording feature greatly assisted in calculating the current velocity, which ranged between 0.5 and 17 cm/sec, and direction (Fig. II-7). The accuracy of the current directions indicated on Fig. II-7 is much improved over directions calculated from a strip chart (Fig. II-5).

Planned Program. The entire system is being designed for unattended, continuous operation. Calibration tests have been performed at the David Taylor Model Basin in Washington. The DWICA unit was taken to Bermuda in March 1964 for tests by the U. S. Navy at Argus Island, with completion of the tests expected during fiscal year 1965.

Tritium Labeling of Organic Materials

An alternative to the Wilzbach self-labeling method[67–69] that is applicable to aromatic materials was recently reported[70–72] and further delineated.[73] In this technique, labeling by hydrogen exchange is effected with a new reagent. It has several advantages over the Wilzbach method in labeling high-molecular-weight hydrocarbons, being faster and cleaner and requiring less tritium to give a product with higher specific activity. The tagged compounds are free of impurities and side products, and recovery procedures are relatively simple. The method is potentially useful in labeling industrially important materials such as coal, hydrogenation and extraction products, and biological substances. It can also be used in structure characterization, particularly to help determine the position of hydrogen atoms in a molecule.

The hydrogen isotope exchange reagent used is tritiated phosphoric acid–boron trifluoride ($TH_2PO_4 \cdot BF_3$), a dense liquid that is made by stoichiometric admixture of tritiated water and P_2O_5, and saturation with BF_3 gas.[70,71] Many organic compounds can be labeled with

the reagent by stirring in a flask at ambient temperature.

Yavorsky and Gorin,[73] working under a Division of Isotopes Development contract at Consolidation Coal Company, defined the labeling range that is possible with the new tritiating reagent. The theoretical limit of tagging, the potential types of organic structures that are susceptible to labeling, and the factors that inhibit or enhance the reaction were described. They also gave methods for tagging unstable compounds as well as comparative data on tagging with tritiated phosphoric acid as opposed to the BF_3 complex. Indirect labeling methods also were developed for difficult materials.

These workers performed a kinetic analysis of the rate of labeling different hydrogen forms in a number of pure aromatic hydrocarbons and with this method showed that equilibrium exchange labeling is achieved in aromatic hydrogen positions and in hydrogen positions adjacent to a tertiary carbon atom. Nuclear magnetic resonance (NMR) data on deuterated cumenes indicated that these tertiary positions act as "gates" for aliphatic labeling but are not themselves labeled. By a combination of equilibrium labeling and kinetics, unknown mixtures can be analyzed to determine their aromatic and tertiary hydrogen content.

Yavorsky and Gorin applied this procedure to structural characterization of coal hydro oil and compared the tritium results with those of NMR analysis.

Theoretical Tagging Limit. The rate of exchange of tritium, when the $TH_2PO_4 \cdot BF_3$ reagent is used, permits in many cases an equilibrium to be reached between the labeled compound and the reagent in a reasonably short time. The equilibrium activity of the tagged compound can be calculated if the distribution between the available hydrogen positions is purely statistical, and the theoretical limit of tagging (ultimate specific activity), S_x^∞, can then be calculated by

$$S_x^\infty = \frac{S_r^0}{\frac{3}{166}\frac{M_x}{N_H} + \frac{W_x}{W_r}}$$

where S_r^0 = initial specific activity of the reagent

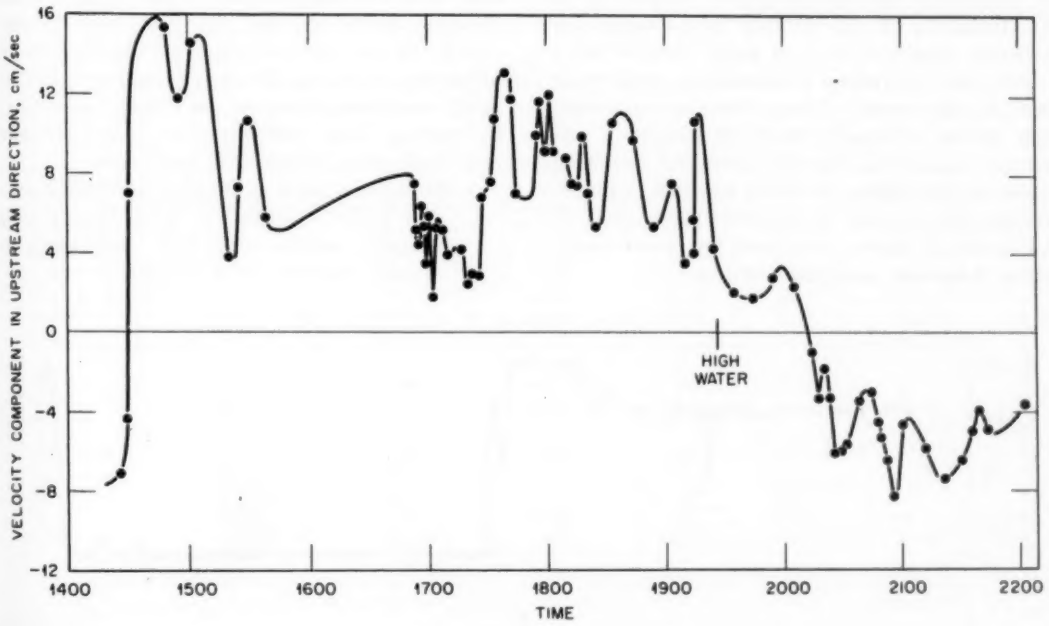


Fig. II-6 Upstream velocity components calculated from DWICA I data in Fig. II-5.

M_x = molecular weight of tracer compound (product)

W_x/W_r = weight ratio of tracer compound to reagent

N_H = number of exchangeable hydrogen positions in tracer compound

The demonstration of equilibrium activity is useful in identifying the exchangeable hydrogen positions in pure compounds. It is potentially useful with unknown materials in analysis for the number of hydrogen atoms of specific types.

Calculation of the number of exchangeable hydrogen positions, N_H, is most precise when a low ratio of tracer compound to reagent is used. Earlier work[70,71] was done with relatively high levels of tracer, and attainment of exchange equilibrium for all aromatic hydrogen positions was shown only for benzene, toluene, tetralin, and anisole. In the more recent study,[73] low levels of tracer were used for better resolution of specific position labeling.

Methods. Most of the Yavorsky and Gorin work was done with pure compounds. The reagent was assayed directly in an ethanol-toluene scintillator solution, whose counting efficiency was determined by use of a tritiated water primary standard. The labeled compounds were assayed by liquid scintillation counting with toluene as the scintillating solvent. The counting efficiency was determined from standard tritiated toluene. Materials that could not be counted in this way were decomposed by dry combustion, and the water collected was counted in an ethanol-toluene solvent. The procedure for recovery of the labeled compound varied with its solubility behavior. The purity was checked by vapor chromatography or, for crystalline solids, by melting point determination. The recovery and purification procedures used were:

1. Liquid Insoluble in Reagent and Water. Decant organic phase and wash tracer with aqueous sodium carbonate and water to remove last traces of reagent.

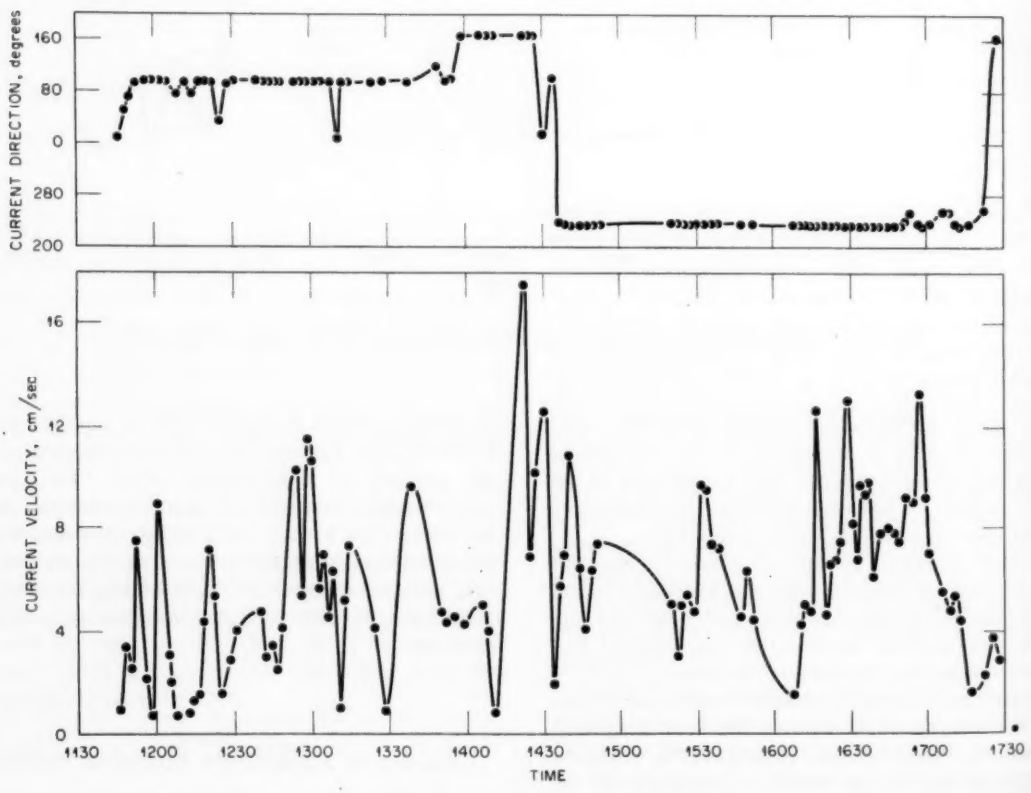


Fig. II-7 Test of DWICA II in Magothy Estuary, Oct. 5, 1962, 1130 to 1730 hr.

2. Liquid Partly or Completely Soluble in Reagent but Insoluble in Water.
   (a) For compounds that are tagged slowly, add water, decant organic phase, and wash with aqueous sodium carbonate and water.
   (b) For compounds that are tagged rapidly, use the same procedure as in (a) but add the compound initially to large excess of water with rapid stirring to avoid exchange of tritium with hydrogen.
6. Volatile Compounds Soluble in Water and Reagent. Recover directly from reagent by vacuum distillation at 0.5 mm Hg and room temperature.

Tagging of Compounds. Neither straight-chain paraffins, such as *n*-octane, nor simple cycloparaffins, such as cyclohexane, were tagged.[70] Aliphatic and naphthenic hydrocarbons that contain a tertiary carbon atom, such as isooctane, decalin, and methylcyclohexane, were tagged.[70] Recent results indicate that the tertiary hydrogen position, as mentioned earlier, does not itself ultimately become labeled with tritium but appears to act as a gate to permit tritium tagging on adjacent carbon atoms (see methylcyclohexane, decalin, and isobutane in Table II-2).

Table II-2 TAGGING OF ALIPHATIC AND ALICYCLIC COMPOUNDS BY USE OF $T\tilde{n}_2PO_4 \cdot BF_3$

Compound	Reaction		Type of mixing	Weight ratio, W_x/W_r	Specific activity, μc/g			N_H
	Time, hr	Temp., °C			Reagent	Tagged compound	Theoretical	
Acetone	3.5	23	None	1.69	41.4	13.8	22.4	6
Heptanone-2	20	23	None	0.0822	41.4	21.7	83.8	5
n-Amyl alcohol	17.5	23	None	0.878	41.4	0.41	24.7	2
Isoamyl alcohol	17.5	23	None	0.869	41.4	0.0	24.9	2
Methyl cyclohexane	216	45	Magnetic stirrer	0.100	41.4	71.3	128.9	8
							76.4	4
							22.1	1
Chloroform	17	23	Same	0.4011	40.7	0.005	15.89	1
	42	23	Same	0.4011	40.7	0.013	15.89	1
							152	8
Isobutane	24	45	Rocker	0.136	40.7	136.0	161.0	9
	551	45	Same		40.7	144.0		
	198	45	Same		40.7	143.0		
	172	45	Same	0.136	40.7	150.0	169.0	10
Decalin	162	45	Magnetic stirrer	0.959	40.7	47.6	30.31	2

3. Liquid Soluble in Reagent and Partly Soluble in Water. Add to excess of water with rapid stirring. Extract with benzene, wash with Na_3PO_4 solution, and distill off benzene.
4. Crystalline Acids Soluble in Reagent. Add excess water. Filter off crystals and dissolve them in dilute NaOH solution. Acidify with HCl and recrystallize.
5. Basic Compounds That Form Salts Soluble in Reagent.
   (a) For liquids, dilute reagent with water and add excess of concentrated NaOH solution. Extract with benzene, wash benzene solution with water, remove water and benzene by distillation.
   (b) For solids, add water and excess NaOH. Extract with ether and recrystallize from ether solution.

Results with heterocyclic sulfur and nitrogen compounds are shown in Table II-3. Thiophene was easily tagged, but the tagging of heterocyclic nitrogen compounds, such as pyridine, was very slow. The deactivating effect of nitrogen apparently also extends to the benzenoid fused ring.

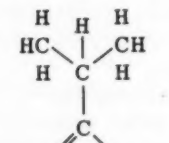
Substituent groups that tend to withdraw electrons from the aromatic ring are known to inhibit substitution reactions, and the more powerful groups, such as nitro and carboxyl, completely suppressed the exchange process at room temperature (Table II-4). Substituent

groups such as alkyl, aryl, hydroxyl, and alkoxyl, which are electrophobic (contribute electrons to the benzene nucleus), tend to activate the exchange process (Table II-5).

The agreement between measured equilibrium activity and that calculated for exchange of all the aromatic hydrogens was excellent for such compounds as benzene, toluene, tetralin, 9,10-dihydroanthracene, and anisole. It was concluded that hydrogens on methyl, methylene, methoxyl, and *n*-alkyl groups attached to the aromatic nucleus do not exchange. Likewise, it was concluded from results with 9,10-dihydroanthracene that methylene bridges between aromatic rings do not exchange.

Results with cumene showed that, if the substituent alkyl group is branched, deep-seated labeling occurs on the alkyl hydrogens. The mechanism is presumably similar to the tagging of branched paraffins and naphthenes—i.e., the tertiary hydrogen acts as a gate to permit extensive tagging of hydrogens on adjacent carbon atoms.

Tagging experiments were also carried out with $D_3PO_4 \cdot BF_3$, and the distribution of the deuterium between the different hydrogen types in cumene was followed by NMR analysis. It was found that the tertiary hydrogen exchanged very slowly, if at all. These results agree with others that indicated that cumene was tagged on 11 positions and not on the equilibrium exchange limit of 12. Eleven hydrogens include all the aromatic and aliphatic carbons but exclude the single hydrogen on the tertiary carbon.



Cumene

This method of tagging with $TH_2PO_4 \cdot BF_3$ gave the following results: (1) Straight-chain paraffins and simple cycloparaffins are not tagged. (2) Aliphatic and naphthenic hydrocarbons that contain a tertiary carbon are tagged, but the tertiary hydrogen is not. (3) Among the heterocyclic sulfur and nitrogen compounds, thiophene is easily tagged but pyridine is tagged slowly. (4) Aromatic compounds are tagged, generally, the extent depending on substituent groups. (5) Substituent groups that withdraw electrons from the ring (e.g., nitro and carboxyl) tend to suppress exchange, whereas electrophobic groups that contribute electrons (alkyl and aryl) tend

Table II-3 TAGGING OF HETEROCYCLIC COMPOUNDS

Compound	Reagent	Reaction		Type of mixing	Weight ratio, W_x/W_r	Specific activity, μc/g			N_H
		Time, hr	Temp., °C			Reagent	Tagged compound	Theoretical	
Thiophene	$TH_2PO_4 \cdot BF_3$	1	23	Magnetic stirrer	0.286	41.4			
	TH_2PO_4	20	23	Same	0.572	63.3	35	34.0	2
5 vol.% solution of thiophene in cyclohexane	$TH_2PO_4 \cdot BF_3$	3	23	Same	0.143	41.4			
	Same	0.005	23	Same	0.143	41.4	13.7	45.7	2
10 vol.% solution of thiophene in cyclohexane	Same	1	23	Same	0.116	63.3	15.0		
	Same	3	23	Same	0.116	63.3	30.3		
	Same	6	23	Same	0.116	63.3	46.3	83.5	4
Pyridine	Same	22	23	None	0.224	40.7	0.07	24.6	1
	Same	16.5	80	None	0.262	37.4	0.7	22.1	1
Pyridine · HCl	Same	22	23	None	0.193	40.7	0.9	26.1	1
Pyridine · BF_3	Same	16.5	80	None	0.267	37.4	1.3	23.8	1
Quinoline	Same	22	23	None	0.294	41.4	0	47.2	4
Pyridine-*N*-oxide	$TH_2PO_4 \cdot BF_3$	45.5	70	None	0.136	40.7	29.8	22.3	1

to activate exchange. (6) Hydrogens on methyl, methylene, methoxyl, and *n*-alkyl groups attached to an aromatic nucleus do not exchange nor do methylene bridges between aromatic rings.

Labeling of Hydro Oil. A narrow boiling fraction of an oil derived from the hydrogenation of coal extract was labeled at 31°C, and an apparent equilibrium specific activity level of 20 μc/g was approached (Table II-6 and Fig. II-8). If the aromatic hydrogens alone were tagged, this activity level corresponds to an aromatic hydrogen content of 12.4% of the total hydrogen. This value was in good agreement with that estimated from NMR spectra. However, prior data with cumene at 31°C showed that the time was insufficient to achieve equilibrium tagging of the aliphatic hydrogens. In addition, the tagging results with the hydro oil at 60°C showed that a much higher level of tagging could be achieved, i.e., 17.2% of the hydrogen was exchangeable. Thus the hydro oil probably contained an appreciable quantity of exchangeable aliphatic hydrogen. A kinetic analysis, made to distinguish between the various types of aromatic hydrogen of differing reactivity as well as between exchangeable aliphatic and aromatic hydrogen, showed fair agreement for the relative amounts of aromatic and exchangeable aliphatic hydrogens (Table II-6). The aromatic hydrogen content was in the range of 9 to 10% of the available hydrogen, or about 3% less than that estimated from the NMR spectra. The precision of the NMR method as applied to unknown complex mixtures has not been definitely established, and no categorical statement could be made without further work as to whether the NMR or tritium method was the more precise. The latter process, in addition to being less expensive, has the advantage of potential application to high-molecular-weight insoluble materials, such as coal and coal extract, which could not be handled by conventional NMR procedures.

The exchangeable aliphatic hydrogen amounts to 7.5 to 8.0 wt.% of the available hydrogen. Only hydrogen atoms on methylene and methyl groups adjacent to a tertiary hydrogen were exchangeable. The total tertiary aliphatic hydrogen content was estimated at 1.5 to 1.6 wt.% of the available hydrogen, assuming that, on the average, each tertiary hydrogen renders five other aliphatic hydrogens exchangeable.

Based on a molecular weight of the oil fraction of 220, one tertiary hydrogen was present for every three oil molecules. Since

Table II-4 TAGGING OF AROMATIC COMPOUNDS (SOME WITH DEACTIVATING SUBSTITUENT GROUPS)

Compound	Reagent	Reaction Time, hr	Reaction Temp., °C	Type of mixing	Weight ratio, W_x/W_r	Specific activity, μc/g: Reagent	Specific activity, μc/g: Tagged compound	Specific activity, μc/g: Theoretical	N_H
Methyl benzoate	$TH_2PO_4 \cdot BF_3$	20	23	None	2.0	41.4	0.0	14.7	3
	Same	20	75	None	1.0	41.4	0.1	22.4	3
Benzoic acid	Same	22	23	None	0.0715	41.4	0.0	81.2	5
Benzaldehyde	Same	20	23	None	0.561	41.4	0.1	16.8	1
Acetophenone	Same	20	23	None	0.548	41.4	37.7	32.5	3
Nitrobenzene	Same	20	23	None	0.641	41.4	0.0	38.2	5
Chlorobenzene	Same	16	23	Magnetic stirrer	0.588	37.4	0.20	29.6	3
	Same	16.5	65	Same	0.588	37.4	20.0	29.6	3
Thiophenol	Same	0.5	23	Same	1.155	37.4	11.0	11.9	1
	Same	17.0	23	Same	1.155	37.4	10.5	20.5	3
Aniline	Same	4.0	75	None	0.109	37.4	1.6	83.8	5
	TH_2PO_4 (16%)	16.0	23	Magnetic stirrer	0.154	19.7	0.0		5
Aniline $\cdot BF_3$	$TH_2PO_4 \cdot BF_3$	22	80	None	0.086	40.7	2.7	105	5
Acetanilide	Same	71	23	None	0.054	37.4	0.9	43.1	5
	TH_2PO_4 (100%)	113.5	23	Magnetic stirrer	0.054	63.3	4.6	70.7	5
	Same	100.5	70	Same	0.054	63.3	48.9	70.7	5
Benzylamine	$TH_2PO_4 \cdot BF_3$	16.5	80	None	0.105	37.4	135	75.8	5
	Same	17	23	None	0.105	40.7	34.3	82.5	5
p-Nitrotoluene	Same	40	75	None	0.535	40.7	8.65	60.6	4

every condensed-ring naphthenic structure of the decalin type would contribute two tertiary hydrogen atoms, two conclusions follow: (1) no more than about one-sixth of the oil molecules could have had decalin type structures, and (2) branched-chain naphthenes and alkyl side chains were present to only a very minor extent. Thus a further advantage of the tritium exchange method for structural characterization is the identification of the presence of tertiary aliphatic carbons; this is not possible with any certainty by the NMR method.

A more positive identification of the slow final tagging rate with the aliphatic hydrogens was established by a comparison of the estimated rate constants with those of pure compounds at different temperatures (Table II-7). The final tagging rate was found to be considerably lower than that for tagging of the least-reactive aromatic hydrogen forms, i.e., the meta hydrogen in toluene. On the other hand, the rate was somewhat higher than the rate of tagging of the methyl groups in cumene. The higher rate would be expected if the tertiary hydrogen were not attached directly to the aromatic ring, as evidenced by a comparison of the rate of tagging of isobutane and cumene (Table II-2).

The categorization of the aromatic hydrogens according to reactivity was inherently less precise than the original split between aromatic and aliphatic forms. (Note the lack of agree-

Table II-5 TAGGING RESULTS WITH AROMATIC COMPOUNDS (SOME WITH ACTIVATING SUBSTITUENT GROUPS)

Compound	Reagent	Reaction		Type of mixing	Weight ratio, W_x/W_r	Specific activity, μc/g			N_H
		Time, hr	Temp., °C			Reagent	Tagged compound	Theoretical	
o-Cresol	$TH_2PO_4 \cdot BF_3$	24	45	None	0.112	40.7	65.1	75.8	4
Anisole	Same	24	45	None	0.112	40.7	80.4	81.2	5
	TH_2PO_4	20	23	Magnetic stirrer	0.532	63.3	30.1	53.0	5
Toluene	$TH_2PO_4 \cdot BF_3$	1	31.5	Platform shaker	0.0925	41.6	10.4	98	5
	Same	5	31.5	Same	0.0925	41.6	36.7	98	5
	Same	54.75	31.5	Same	0.0925	41.6	97.0	98	5
	Same	1	45.0	Same	0.0925	41.6	18	98	5
	Same	19.75	45.0	Same	0.0925	41.6	96.3	98	5
	Same	24	45.0	Same	0.0925	41.6	97.4	98	5
	TH_2PO_4 (100%)	1	23	Stirred flask	0.170	63.3	0.1	86.4	5
	Same	24	24	Same	0.170	63.3	5.2	97.9	5
Benzene	$TH_2PO_4 \cdot BF_3$	1	21	Platform shaker	0.0935	41.6	0.9	126.6	6
	Same	100	21	Same	0.0935	41.6	90.9	126.6	6
	Same	1	60	Same	0.0935	41.6	17.1	126.6	6
	Same	50	60	Same	0.0935	41.6	127.1	126.6	6
Cumene	Same	24	25	Magnetic stirrer	0.123	41.6	80.7	85.8	6
	Same	0.5	31	Platform shaker	0.091	33.4	1.34	122.6	12
	Same	360	31	Same	0.091	33.4	99.7	122.6	12
	Same	1	60	Same	0.091	35.4	12.29	129.9	12
	Same	100	60	Same	0.091	35.4	116.23	129.9	12
10 wt.% solution of naphthalene in cyclohexane	Same	7	23	Mechanical stirrer	0.199	1400	1440	2865	8
2 wt.% solution of 9,10-dihydroanthracene in cyclohexane	Same	20	23	Magnetic stirrer	0.107	600	1200	1200	8
	Same	44	23	Same	0.107		1040		8
Tetralin	Same	0.5	23	Mechanical stirrer	1.97	1400	151	545	4
	Same	5.5	23	Same	1.97	1400	521	545	4

ment between the breakdown estimated at 31 and 60°C.) There were aromatic hydrogen forms of widely varying reactivity present, although the qualitative split was uncertain.

Judged from the rate constants, the least-reactive aromatic hydrogen had a reactivity at least as high as the ortho and para hydrogens in cumene. The most reactive form may be representative of condensed-ring aromatics, which qualitatively were known to label more rapidly than single-ring aromatics.

Yavorsky and Gorin concluded that the tritium labeling data were not inconsistent with the division into condensed- and single-ring aromatic forms as determined by NMR data.

Table II-6 ANALYSIS OF RESULTS OF TAGGING HYDRO OIL CUTS

[Oil Data: Boiling Point at 10 mm Hg, 160–167°C (Corrected to 306–316°C at 760 mm Hg). Ultimate Analysis, Wt.%: H, 10.59; C, 88.57; N, 0.38; O, 0.38; S, 0.08. Molecular Weight: 220]

Forms of hydrogen	Hydrogen distribution, % of total: From kinetics of tritium labeling at 31°C	60°C	From NMR analysis
Total aromatic	9.6	9.1	12.5
Unreactive aromatic	3.5	6.1	
Intermediate aromatic } Reactive aromatic }	6.1	3.0	
Total exchangeable	19.2	18.2	
Single-ring aromatic			6.3
Condensed-ring aromatic			6.2
Exchangeable aliphatic	7.5	8.0	
Tertiary aliphatic	1.5	1.6	

Kinetics of Exchange Labeling. The kinetics of the isotopic exchange reaction between deuterobenzene and tritiobenzene and toluene in ~81% aqueous sulfuric acid has been studied by Olsson.[74] He found that the reaction rate, with relatively vigorous agitation, was adequately expressed in his experiments as a homogeneous reaction taking place between the acid and the small amount of hydrocarbon dissolved in that phase.

Yavorsky and Gorin examined his three suggested mechanisms for the exchange reaction—reaction in the acid phase, in the hydrocarbon phase, or at the interface between these phases. They found that for all types of mechanisms the reaction kinetics followed a "pseudo" first-order law. That is, a semilogarithmic plot of the quantity $1/(1-S_x/S_x^\infty)$ vs. time should give a straight line whose slope is the pseudo first-order constant, k'. S_x is the measured specific activity of the tracer compound in millicuries per gram, and S_x^∞ is the value after equilibrium labeling. The relation of k' to the parameters of the system varies with the particular mechanism chosen. These relationships could be applied to determination of the distribution of hydrogen forms by first determining their respective rate constants in an unknown mixture (see below).

From Yavorsky and Gorin's kinetic studies with benzene, a purely homogeneous reaction could be ruled out in either phase or at the interface if it is assumed that the observed rate is entirely determined by the chemical reaction rate. Although the theoretical basis and results are not presented here (see Ref. 73), the details of two series of experiments are included. The first was carried out in a stirred flask with a relatively low weight ratio, and the second in a platform shaker with a high ratio, of reagent to compound. If the reaction had been purely homogeneous, the rate constants for the two series of experiments should have agreed; they did not, so the reaction could not have been homogeneous. It was concluded that mass transport, and thus mixing, had a definite effect on the rate constants. Also ruled out was a reaction in the acid phase with partial mass-transport control.

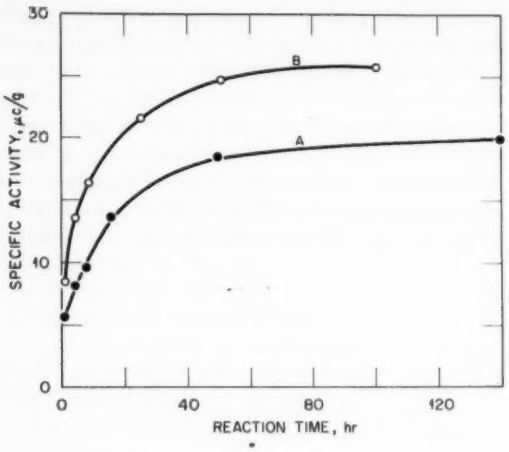


Fig. II-8 Tritium labeling of coal extract hydro oils by use of $TH_2PO_4 \cdot BF_3$ at two temperatures. Two separate experiments: *A*, initial specific activity of reagent, 27.9 μc/g; ratio of the weight of reagent to tracer compound, 137.3, 31°C. *B*, 26.6 μc/g, 77.65, 60°C.

It seemed likely, then, that the reaction was a surface one. The observed rate appeared to be determined largely by the chemical reaction rate when vigorous agitation and low temperatures were used. At high temperatures, particularly with insufficient agitation, the rate of mass transport becomes important in determination of tagging rate.

These benzene data were compared with similar kinetic results obtained with toluene and cumene (Table II-7). It was noted that the isopropyl group had a relatively mild activating effect compared to the methyl group. The rate constant for tagging of the ortho and para hydrogens was 2.5 to 4 times less in cumene than in toluene, although the rate was still 1.3 to 2 times greater than that for the tagging of benzene.

The initial activation energy for toluene, calculated from an Arrhenius plot at 21°C, is 11.6 kcal/mole and decreases to about 10 kcal/mole at 45°C. The true activation energy for tagging of the ortho and para hydrogens in toluene was considerably lower than for benzene, i.e., 12 vs. 18 kcal/mole. The lower value was expected since the observed rate constant for toluene was 5 to 7 times larger than that for benzene.

The higher value for the rate constant obtained for toluene tagging indicates that mass transport played an even larger role in the tagging rate determination than for benzene. The fact that the Arrhenius plot showed less curvature seemed to belie this assertion, but the smaller curvature was explained by the much smaller difference between the activation energies of reaction and diffusion for toluene, i.e., only about 2 kcal/mole vs. about 10 kcal/mole for benzene.

The ratio of the ortho and para rate to the meta rate is only about 3:1, whereas a ratio of 44:1 was found by Gold and Satchell[75] in the exchange of deuterotoluene with aqueous sulfuric acid and a ratio of 40:1 by Olsson[74] in the exchange of tritiotoluene with aqueous sulfuric acid. The observed ratio of the ortho and para to meta rates was presumed lower than the actual ratio of the rate constants if the rate of mass transport partly determines the observed

Table II-7 PSEUDO FIRST-ORDER RATE CONSTANTS FOR TAGGING OF DIFFERENT COMPOUNDS

(The $TH_2PO_4 \cdot BF_3$ Reagent Was Used with Mild Stirring by Platform Shaker)

Compound	Temp., °C	First-order rate constant	Rate constant relative to benzene
Benzene*	21	0.0086	1
	31	0.026	
	45	0.060	
	60	0.11	
Cumene			
Methyl	31	0.0033	0.13
	60	0.022	0.2
Meta H	31	0.0058	0.22
	60	0.045	0.4
Ortho, para	31	0.034	1.3
	60	0.23	2.1
Toluene			
Meta H	21	0.025	2.9
	31	0.042	1.6
	45	0.109	1.8
Ortho, para	21	0.064	7.4
	31	0.13	5.0
	45	0.274	4.6
	60	0.6	5.5
Hyro oil			
Aliphatic H	31	0.011	0.4
	60	0.043	0.4
"Unreactive" H	31	0.058	2.2
	60	0.30	2.7

*Here the rate constant

$$k'' = \frac{\text{slope}}{\left[1 + \frac{1}{r}\left(\frac{Nx}{Nr}\right)\left(\frac{Mr}{Mx}\right)\right]}$$

All other rate constants are calculated with the assumption that $r = \infty$; see kinetics section, page 239.

rate. But Yavorsky and Gorin showed that the ratio was lower than 40 : 1 in their system, even with mass transport.

The ratio of the meta tagging rate to the benzene tagging rate was 2.9 : 1, which is in good agreement with the corresponding ratio of 2.6 : 1 found by Olsson.

The relative activities of the $TH_2PO_4 \cdot BF_3$ and TH_2PO_4 reagents were compared by determining the rates of tagging of toluene with each one. The rate constant for the $TH_2PO_4 \cdot BF_3$ reagent was 230 times greater than that for TH_2PO_4.

Application To Determining Distribution of Hydrogen Forms. The kinetic analysis technique just discussed can be applied to the determination of the distribution of hydrogen forms by first finding out their respective rate constants in an unknown mixture. The method is thus potentially a powerful one for the structural characterization of unknown materials. The method is more easily applied where a very high ratio of reagent to compound is used. If a substantial difference exists between rate constants, a "peeling-off" procedure may be used similar to that used in activation analysis or in any other set of simultaneous rate processes. The derivation of equations for the following summary of the procedure is described in detail by Yavorsky and Gorin.[73]

Consider, for example, the case where the least-reactive form of hydrogen has a rate constant no greater than one-third that of the next least-reactive form. After a period of time, when the labeling reaction is completed to the extent of 99% or better for the other forms of hydrogen, the exchange will be less than 80% completed with the least-reactive hydrogen form. The rate constant for the least-reactive hydrogen form can be calculated by

$$\frac{S_x}{S_x^\infty} = \frac{\Sigma\, n_i (1 - e^{-k_i' t})}{\Sigma\, n_i}$$

where n_i is the number of atoms of type i per mole of hydrocarbon, n_x is the number of hydrogen atoms per mole of hydrocarbon when only one type is present, and k_x' is the rate constant. Under conditions where all the exponential terms have essentially decayed to zero except the one representing the least-reactive form, this equation may be rewritten as

$$\ln \frac{1}{1 - S_x/S_x^\infty} = k_x' t + \ln \frac{\sum_1^x n_i}{n_x}$$

The proportion of the least-reactive hydrogen may be determined by plotting $1/(1 - S_x/S_x^\infty)$ vs. time on a semilogarithmic scale. The data at the longest reaction times should approach a straight line which, when extrapolated to zero time, gives an intercept equal to $\left(\sum_1^x n_i\right)/n_x$, i.e., the ratio of the total hydrogen content to that of the least-reactive hydrogen form. The slope of the line is used to determine k_x'.

The rate constant for the least-reactive form can be used to subtract the contribution of this hydrogen form to the total activity. The specific activity of the reagent, S_r, due to the remaining hydrogen forms, may then be used to compute

$$\frac{1}{1 - S_r \Big/ \sum_1^{x-1} S_i^\infty}$$

which is plotted on a semilogarithmic scale vs. time. The ordinate intercept of the straight line through the points representing long times now determines the ratio $\left(\sum_1^{x-1} n_i\right)/n_{x-1}$, where n_{x-1} refers to the number of hydrogen atoms per mole of the second least-reactive form. The procedure can be repeated until all the hydrogen forms are accounted for. However, precision lessens with each repetition because errors accumulate in the estimation of the rate constants. An example of this procedure in determination of the hydrogen forms in hydro oil is shown in Fig. II-9.

There is good agreement between the data at 31 and 60°C in the extrapolation to determine the proportion of the least-reactive, i.e., the aliphatic, hydrogen. Further extrapolation to determine the distribution between the various aromatic hydrogen forms does not, however, show good agreement between results at the two temperatures. The actual quantitative split (Table II-6) between the different aromatic hydrogen forms therefore has only qualitative significance. Nevertheless, at least three different aromatic hydrogen forms are detectable by this technique.

Further development of the procedure for structural characterization of natural products is possible. The method is susceptible to substantial automation, particularly with introduction of computer programs for calculation of the distribution of hydrogen forms, but its precision should be improved. One method of ac-

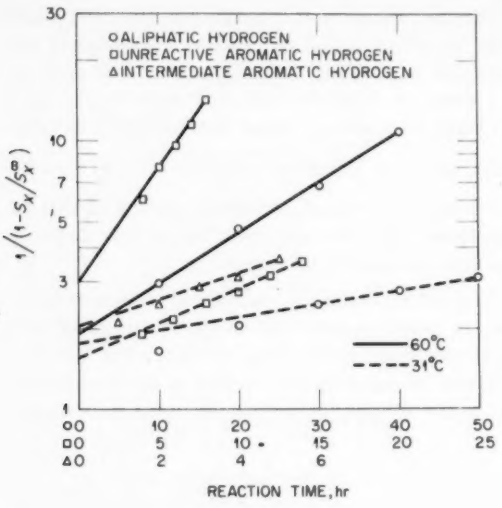


Fig. II-9 Extrapolation plot for determination of different hydrogen forms in coal hydro oils.

complishing this would be to carry out the tagging experiments under conditions of more vigorous agitation, and thus eliminate mass transport between phases as a factor contributing to the observed rate. This procedure would give a greater spread between rate constants, which would help identify the individual forms.

Stable Isotope–Activation Analysis Tracing

In many industrial installations both potable and nonpotable water systems are used, and it is sometimes necessary to make emergency interconnections–for example, to maintain emergency water pressure for a fire-protection system. Epidemics of waterborne diseases have been caused by backflow of contaminated water through cross connections between two such systems. Present methods to prevent cross-contamination include: (1) completely separate potable and nonpotable water-pressure systems, (2) use of potable water for nonpotable systems through air-gap separation installations, (3) reduced-pressure backflow preventers[76] in cross-connecting lines, and (4) use of double check-valve assemblies in cross-connecting lines.

Reduced-pressure backflow preventers had been tested numerous times; however, none of the available data seemed appropriate to the tight shutoff and intermittent flow requirements of nuclear research and batch operations, nor were the data suitable as guides for health physicists in considering the safety of such devices in radiochemical processes. The following tests were set up to establish the reliability of this device under the very stringent requirements of a nuclear installation.

Baird, Sanford, and Cristy[77] recently used a stable isotope of manganese as a tracer in conjunction with activation analysis to test a reduced-pressure backflow preventer at Oak Ridge National Laboratory (ORNL). Radioactive tracers had originally been proposed for this test. However, a stable isotope–activation analysis tracing method using manganese appeared to have the following advantages over the radioactive tracer method:

1. A higher ionic concentration of the stable-isotope tracer solution could be used than with a radioactive tracer, with the result that the backflow would be more readily detectable.
2. The test apparatus could be assembled in a more convenient location, where health physics supervision was not required.
3. No shielding of the apparatus or samples, or other precautions necessary with radioactive compounds, would be required.
4. The apparatus would not require decontamination after the tests were completed.
5. Neither the length of the testing nor the time elapsed between sampling and analysis would require consideration.

Test Procedure. The tests consisted in confining a manganese nitrate solution in the discharge end of the device, filling the supply and relief zones with potable water, and conducting tests to simulate malfunctions of the water system that might cause backflow (Fig. II-10). If the manganese concentration in the supply zone after the test was greater than that in a potable water sample taken before the test, backflow would be indicated. The test procedures were very carefully developed to prevent the chemical solution in the discharge zone from contaminating the upstream zones, either during the filling before testing or during sampling after testing.

Thorough efforts were made to maintain integrity of the samples. The drain tubes from the different zones were washed and then rinsed with distilled water prior to sampling. In sampling, the relief and supply zones were drained

completely into 2- and 1-gal bottles, respectively, which held the entire contents of each zone. During most of the tests, a 2-gal bottle was kept under the relief drain outlet to retain the water discharged when this valve opened. This water was combined with the contents of the relief zone after the test. All sample bottles were new polyethylene bottles, well rinsed with distilled water prior to use.

In preliminary tests the solutions in the relief and supply zones were found to be picking up manganese from the construction materials. eliminated. The discharge zone did not have to be manganese-free since it was used to contain the manganese chemical solution.

A saturated solution of manganese nitrate was used as the tracer to increase the overall accuracy and sensitivity of the tests. By analysis, the average value of the added manganese for all five tests was 126 mg/ml, or 1.3×10^8 ppb.

The effect of manganese pickup from construction materials was reduced by running each test twice, first with water confined in the discharge zone and then with the manganese

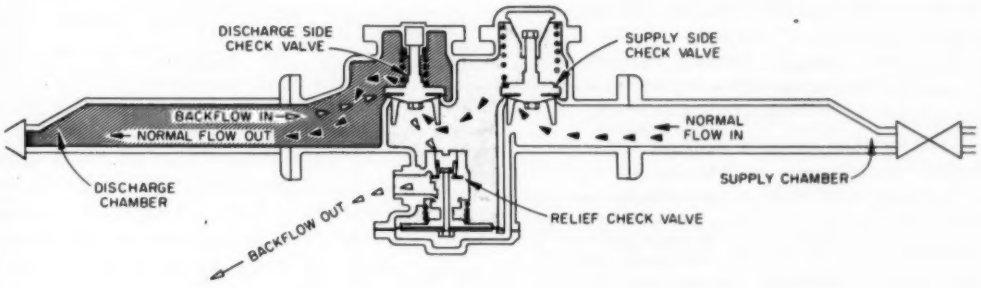


Fig. II-10 Reduced-pressure backflow preventer and test apparatus.

The test assembly had been constructed with materials most readily at hand, and, since the actual test chemical solution had not been definitely chosen at the time of construction, no thought was given to making a manganese-free assembly. The discharge and supply chambers were stainless steel with a probable manganese content of 2%, and iron pipe fittings contained 0.03 to 0.65% manganese. According to the seller, the backflow preventer casting itself contained no manganese.

The two stainless-steel springs in the relief zone were copper plated to a thickness of 0.0045 in. to minimize water contact with manganese-containing metals. The supply side chamber was rebuilt with a brass pipe and brass flange with brass nipples. Construction was all brazed, the brazing compound being 72% silver–28% copper. In the relief and supply zones, fritted stainless-steel snubbers were removed from the gage lines, and brass fittings were substituted for iron. Manganese buildup then decreased to about one-fourth its former value, although later tests showed that the effect of construction materials had not been entirely reagent confined in this zone. Corresponding samples had the same residence times in the device and were subject to the same agitation conditions. Thus the pickup of manganese from construction materials by the blank samples probably was very close to that of the actual samples, and time and agitation were eliminated as variables.

Analytical Procedure[76]

Each sample was neutron irradiated in plastic bottles in the ORNL Graphite Reactor for 4 hr and was then returned to the laboratory for processing. In each test a solution of manganese carrier (as manganese nitrate, containing 10 mg/ml) was added to the solution along with holdback carriers of copper, iron, sodium, and barium. A known amount of cobalt carrier (cobaltous nitrate, 10 mg/ml) was sometimes added as a carrier when cobalt was also to be determined. This initial solution was made basic with either 2*M* sodium hydroxide or 2*M* ammonium hydroxide. (Owing to the chemical reaction of NH_4OH with the added peroxide, sodium hydroxide was preferred.) Upon the addition of base, manganous hydroxide was formed (a light-pink precipitate), 10 drops of 30% solution hydrogen peroxide was added dropwise, and the solution was

stirred until manganese dioxide was completely precipitated. Then the solution was heated to near boiling to coagulate the precipitate and centrifuged, and the separated manganese dioxide precipitate was washed with 6*M* nitric acid. After the precipitate had been dissolved in 2 ml of formic acid, 5 ml of concentrated nitric acid was added, and the solution was heated to boiling. Solid potassium chlorate was added cautiously in small amounts; and, after each addition, the solution was boiled; in all, sufficient potassium chlorate was added to precipitate the manganese dioxide completely. The mixture was centrifuged, and the precipitate of manganese dioxide was washed with 2 to 3 ml of concentrated nitric acid and filtered, washed, dried, and mounted for counting.

The activity of the precipitate of the manganese carrier and 2.6-hr Mn^{56} was determined by gross gamma counting. Gamma spectrometry was used to determine the purity of the precipitates prepared by the radiochemical separations.

Results. The final tests (Table II-8) showed that there was no detectable backflow. Although a slight increase in concentration occurred in the supply zone during the tests with vacuum and a water hammer on the downstream side, the differences shown fall within the reproducibility of the analytical method. Each test produced one set of samples, and each sample was analyzed in duplicate.

Manganese was used as the tracer element because its concentration in potable water is only about 3 ppb, highly concentrated reagent solutions can be prepared, and activation analysis techniques can detect concentrations of 0.2 ppb.

In reviewing the data, it should be recognized that two criteria must be satisfied simultaneously to prove backflow:

1. The concentration of manganese in the supply zone must be greater in the test using manganese nitrate reagent than in the blank test using water as a reagent.

2. In each test using the manganese nitrate reagent, the concentration of manganese in the relief zone must significantly exceed that in the supply zone.

Table II-8 TESTS OF REDUCED-PRESSURE BACKFLOW PREVENTER

Reagent	Test	Manganese, ppb		Backflow
		Relief zone	Supply zone	
$Mn(NO_3)_2$	Ionic diffusion	6.3 – 6.0	5.0 – 5.3	No
Water	Ionic diffusion	10.5 – 10.4	12.0 – 11.0	
$Mn(NO_3)_2$	Vacuum	4.9 – 5.0	1.0 – 1.0	No
Water	Vacuum	0.6 – 0.6	0.9 – 0.9	
$Mn(NO_3)_2$	40 water hammers on supply side	4.5 – 4.6	5.1 – 5.0	No
Water	40 water hammers on supply side	1.5 – 1.6	2.7 – 2.7	
$Mn(NO_3)_2$	Low pressure	7.4 – 7.0	19 – 22	No
Water	Low pressure	15 – 16	21 – 22	
$Mn(NO_3)_2$	40 water hammers on discharge side	3.4 – 3.6	3.0 – 3.0	No
Water	40 water hammers on discharge side	2.5 – 2.6	2.7 – 2.8	

Obviously, under the first criterion, unless the test with manganese solution results in more manganese in the supply zone than that shown by the blank, only background has been observed and no backflow could have occurred. However, the mere fact that after a test the supply zone contains manganese in excess of the blank does not necessarily prove that backflow through the preventer has occurred. True backflow through the preventer must first traverse the intermediate relief zone and then enter the supply zone, where it would be diluted. Therefore, if backflow exists, the chemical concentration must be higher in the relief zone than in the supply zone. In fact, it should be high enough to account for any increase in the supply zone concentration after dilution.

The relief zone is considered a contaminated zone by the manufacturer of the backflow preventer; hence the presence of manganese in this region is not detrimental, especially since this zone is maintained at a lower pressure than the supply zone.

Use of Isotopes in the Food-Canning Industry

By Walter A. Mercer* and Jack W. Ralls†

This review describes the use of isotopes in research on quality control in the food-canning industry. By definition, this industry comprises companies that pack foods in hermetically sealed containers, the contents being preserved by a thermal process. Processing steps are: washing, sorting and grading, filling and sealing containers, and cooking.

The nation's modern canning industry includes approximately 2200 plants, located in 49 of the 50 states as well as in Puerto Rico, operated by some 1800 separate companies.[79] In 1962 the industry produced 756 million cases, containing about 26 billion containers, of food with a retail value of $5.2 billion. Each day, on an average, consumers of this nation open and use the contents of approximately 75 million cans of food products of all kinds for a per capita consumption of about 138 lb/year.

Research for the food-canning industry is done in five types of organizations:

1. Government laboratories such as those of the U. S. Department of Agriculture
2. Academic institutions, represented by departments of food science and technology at colleges and universities
3. Research laboratories of the larger canning companies, container manufacturers, and supplier industries
4. Trade association research laboratories, such as those of the National Canners Association
5. Contract research institutes or foundations

Many of these laboratories are licensed by the AEC Division of Licensing and Regulation to use radioactive isotopes in research.

The major portion of this review is devoted to work done by the National Canners Association since this work is available for publication and the authors are familiar with it. Much of this work is sponsored by the AEC Division of Isotopes Development. The National Canners Association has been interested in the utility of isotope technology to the food-canning industry since the inception of programs to develop peaceful uses of nuclear energy. In 1955 they participated in the Nevada Flats tests of the effect of nuclear weapons on conventional food containers. An excellent account of the highlights of this study appeared recently.[80]

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Research on Raw Food and Containers

The quality of the raw food prior to processing is a major factor in final product acceptability, and research on methods to improve this quality is continually conducted by government and industrial agricultural experiment stations. An example of such research is the use of P^{32} to trace the uptake of fertilizer phosphorus in tomato plants.[81] This isotope has also been used to measure root distribution and development in carrots, snap beans, onions, potatoes, and peppers.[82] In the field of poultry nutrition, a recent news item[83] describes the feeding of $1000 worth of a radioactive feed additive to a single chicken to study the metabolism of the additive.

The Bureau of Commercial Fisheries, U. S. Department of the Interior, has used a gold-plated Alnico-5 slug, plastic-coated, activated with 10 μc of Co^{60} to tag Alaskan herring from spawning grounds to commercial reduction.[84] The slug is placed in the fish's stomach at spawning and recovered some four months later by a magnetic device in the reduction factory.

Phosphorus-32 has also been used in studies on the efficiencies of methods for cleaning dairy equipment.[85]

A novel use of a radioisotope in a can manufacturer's laboratory was labeling of *Escherichia coli* bacteria by growing them in a medium containing phosphate-P^{32} and using the culture to evaluate the efficiency of bacterial removal, by various sanitation procedures, from several different materials used in the construction of food-processing equipment.[86]

Detection of leakage of closed-can side seams by monitoring the loss of a radioactive gas such as Kr^{85} has been suggested[87a] in research on can improvement.

Quality Control

The major use of isotopes in quality control during food processing is in density determinations. In the production of tomato paste, a

density gage containing 200 mc of Cs^{137} is used by a major producer of tomato products.[87b] The radiation source and measuring cell are mounted on the discharge piping of a turbofilm evaporator. The recorder-controller receives from the measuring cell an electrical signal that is proportional to the density of the product flowing through the pipeline. This signal is used to activate the density controller of the finished product. A similar device has been discussed in a Russian publication.[87c]

Autoradiography of Crop Samples Treated with Radioactive DDT

DDT-C^{14} and DDT-H^3 were used in studies on means for decreasing pesticide residues on marketed raw food by application of a method developed to study the fate of pesticides applied to growing crops. Spinach, carrots, tomatoes, and cauliflower were selected in order to cover the range of problems encountered in processing. In the case of spinach, preliminary results suggest that trimming older leaves from bunches of spinach before marketing would decrease the pesticide level in the marketed food. A series of autoradiographs (Fig. II-11) of spinach leaves, made at various times after being sprayed with DDT-C^{14}, showed progressive concentration of activity in the older leaves as the plants matured, partly because the younger leaves have a proportionally larger growth than the older leaves and partly because the younger leaves would have a greater new tissue dilution of the original activity level. The roots of spinach plants showed radioactivity even when the soil was protected against contamination by sprayed DDT-C^{14}; this is a result of the higher degree of absorption and translocation of the activity associated with the higher metabolic activity of the younger leaves.

Preliminary tests on the usefulness, as a tracer, of a DDT-H^3 preparation in which 90% of the activity was in the potentially exchangeable benzylic hydrogen showed that purified DDT recovered from tomato and spinach plants has the same specific activity as that originally applied to the plants. DDT-H^3 was prepared by the Wilzbach technique and extensively purified to remove high-specific-activity impurities. The original 1-g sample, with an activity of 31.7 μc/mg, was diluted with 10 g of nonradioactive DDT and purified until 92% of the activity coincided with the DDT spot in thin-layer chromatograms. The 3.3-g product, with an activity of 0.63 μc/mg, was made into a 1% DDT emulsion and sprayed onto young tomato plants, 50 mg of nonradioactive and 1.73 mg of DDT-H^3 per plant. The plants were then grown 15 days in a chamber, after which the DDT was extracted from the total aboveground portions. It was purified by thin-layer chromatography, and its specific activity was compared with that of the original material. The study with spinach was similar except that the plants were grown for 88 days after being sprayed.

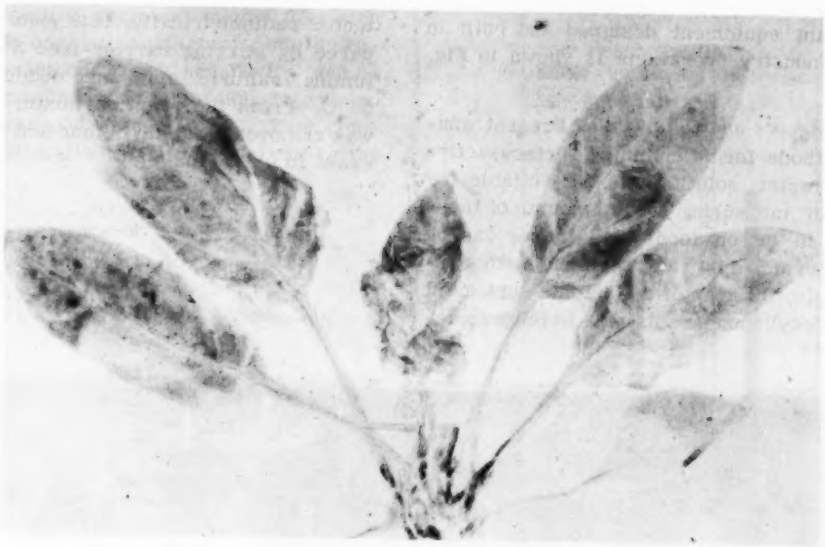
When DDT-H^3 was applied to spinach plants grown in a specially constructed chamber at the maximum rate, 6 lb/acre, recommended by agricultural bulletins, only 10% of that sprayed on remained after 26 days:

Time in chamber, days	Residual DDT	
	ppm	%
0	147	100
8	81	55
12	47	32
16	29	20
21	20	14
26	15	10

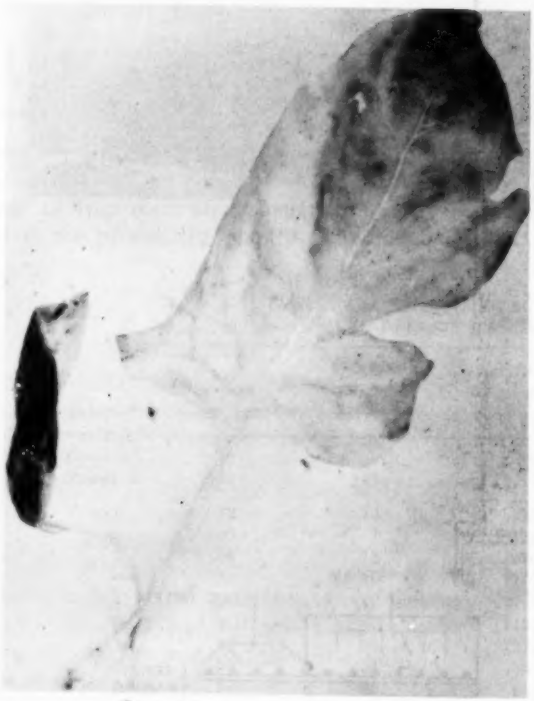
These plants were only about one-third the size of commercial field plants, and the residue levels at harvest were therefore three times as large as those to be expected in commercial spinach.

Research on Food Washing

Radioactive isotopes have been profitably used in studies of food washing. Because of the growing emphasis on cleaner food, the use of wetting agents in processing, the use of detergents to remove organisms and pesticides, and the need to remove the detergents, an extensive series of studies on precanning food processing was undertaken. The investigations were made both to evaluate the efficiency of present commercial food-washing procedures to remove residues and to develop information that could be used by industry to improve food-cleaning methods, rather than to develop radioisotopic tracer techniques for routine monitoring of residue removal from foods. Radioactive materials cannot be used with food intended for human consumption unless they and their decay products have extremely short half-lives.



(*a*)



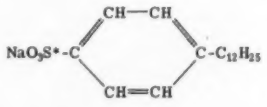
(*b*)

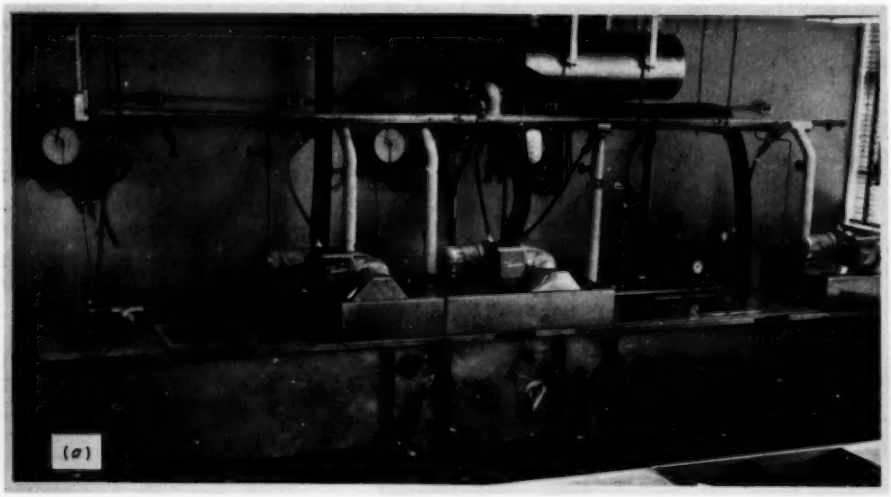
(*c*)

Fig. II-11 Spinach harvested after (*a*) 0 days, (*b*) 23 days, and (*c*) 35 days. The autoradiographs were prepared with exposure times of (*a*) 46 hr, (*b*) 144 hr, and (*c*) 168 hr.

Pilot-plant equipment designed and built to duplicate industry operations is shown in Fig. II-12.

Wetting Agents and Detergents. Present analytical methods for determining surface-active agents in water solution are not suitable for detecting or measuring trace amounts of these materials in or on foods, but traces can be readily determined by radiochemical methods.[88] For example, 0.2 ppm of the anionic surfactant sodium dodecylbenzene sulfonate (ABS) was detected radiometrically. This material was prepared by stirring carrier-free S^{35} sulfate with fuming sulfuric acid and dodecylbenzene at 50°C. From the reaction mixture the product was removed with ethyl ether and further processed to yield ABS:





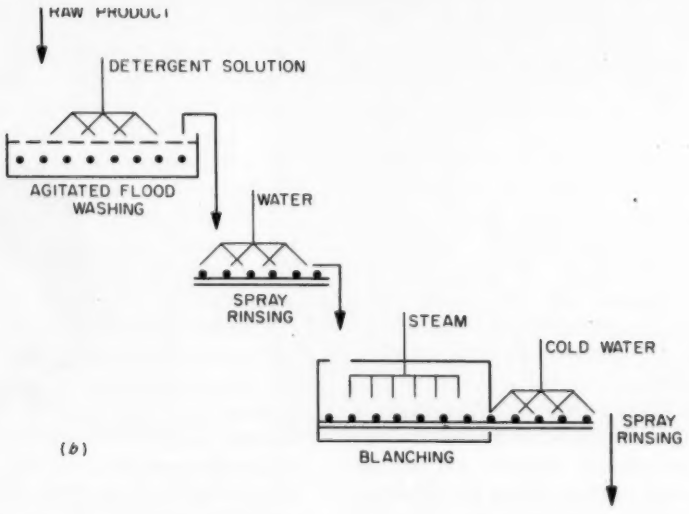
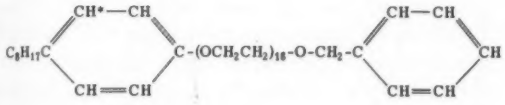


Fig. II-12 Pilot-plant (*a*) installation and (*b*) process for studying removal of surface residues from food products.

No useful sensitive chemical method has been developed for nonionic surfactants, but the radiochemical method has a sensitivity of 0.04 ppm for the nonionic surfactant polyethoxylated octyl phenol benzyl ether (PEPB). This compound was labeled with tritium for use in the studies:



Wetting Agents in Peeling with Lye. Wetting agent is added to the caustic solution used to peel apricots, peaches, and tomatoes. Radioactive ABS was used to show that some of the wetting agent diffuses into peripheral tissues of the peeled fruit but that, with adequate rinsing, less than 0.05 ppm of wetting agent remains (Fig. II-13 and Table II-9). This is not considered significant from the standpoint of food adulteration. By using the radioisotopic technique, it was also possible to show that the use of wetting agents results in more uniform peeling and higher product yield and permits use of lower caustic concentrations and smaller volumes of rinse water.

Detergent Washing of Asparagus. Evaluation of the effectiveness of detergent washing of asparagus is important since asparagus as received at the processing plant is contaminated with large numbers of bacterial spores present in field soil, and their removal during washing can be used as a measure of the effectiveness of the operation. In addition, such physical features of asparagus as the bracts and clustered heads protect contaminants from detergent action and interfere with flushing away by water of the contaminants and residual detergent.

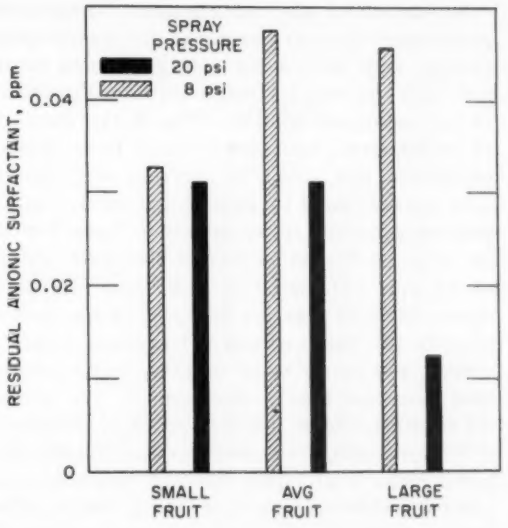


Fig. II-13 Effect of fruit size and spray-rinse pressure on anionic surfactant remaining on lye-peeled cling peaches.

Table II-9 CONCENTRATION OF SURFACTANT AND SODIUM RESIDUE IN LYE-PEELED, WASHED TOMATOES

Sample*	Sodium found, ppm	Residue excess, ppm	Activity in 10-g sample, counts/min	ABS residue, ppm	Sodium/ABS ratio
Control	49				
Standard	196	147	1372.4	697.0	213
Test 1	62	13	38.1	0.019	667
2	56	7	19.8	0.010	714
3	64	15	45.0	0.023	667
4	98	49	114.8	0.058	833
5	61	12	76.0	0.039	313
6	81	32	115.4	0.059	555
7	85	36	122.6	0.062	588
8	70	21	30.4	0.015	1430
9	78	29	53.9	0.027	1112
10	81	32	156.0	0.079	400
Average of tests	73.6	24.6	77.2	0.039	729

*Control samples were hand-peeled tomatoes. The standard reference sample contained a known quantity of radioactive peeling solution.

By means of the radiochemical method, the percentage of spores removed was shown to increase with decreasing detergent foam height and with increasing temperature and pressure of the detergent solution (Fig. II-14). Removal of radioactive detergent residue from washed asparagus was shown to increase very rapidly with time from 0 to 10 sec and fairly rapidly with increase in spray pressure from 5 to 20 psi (Fig. II-15). Some bound detergent (a total of 1.5 ppm calculated as ABS) from composite spear samples was not removed by the rinsing (Fig. II-16). The amounts of bound detergent involved, too small to be detected by techniques less sensitive than radiochemical, are thought not to constitute an industry problem. However, it is interesting that detergent apparently diffused more easily into the open tissue of a cut surface. Fifty-six percent of the total radioactive residue was found in a cross section of the spear butt that represented only 7.4% of the total spear weight; one face of this cross section was the cut made, previous to the detergent wash, to trim the spears to canning length.

Detergent Washing of Olives. The pickling of olives in brine solution is one of the oldest food-preservation practices. Today, olive growing is an important horticultural practice in many of the semiarid regions of the world, that in the United States being concentrated in Arizona and California. Green olives delivered to the processing plants are not usually washed before storage in brine. However, problems resulting from pesticide and other residues indicate that washing should be investigated; olive growers and processors are in agreement.

Studies made with radioactive detergent on Sevillano olives obtained directly from the orchard indicated that washing prior to putting them in brine decreases shriveling of the skin (Fig. II-17). The concentration of detergent in the olives at various stages during processing (Table II-10) shows that detergent washing of olives does not create a significant residue problem. Brines containihg 1000 ppm of detergent could not be used in industrial practice (residue level 13.9 ppm).

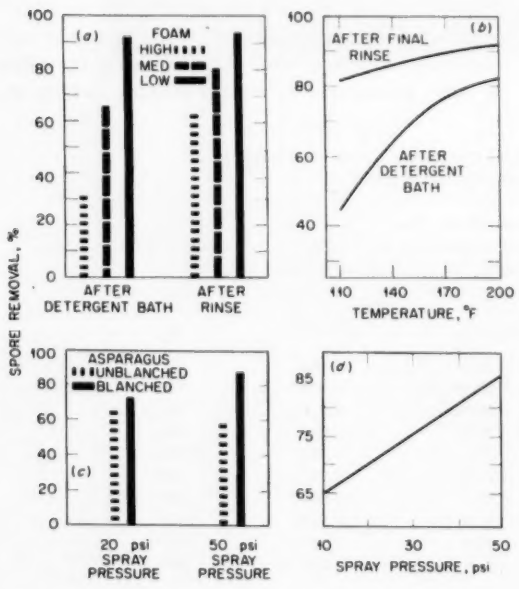


Fig. II-14 Effect of (*a*) foaming characteristics, (*b*) temperature, and (*c*) pressure of detergent solution spray in removing bacterial spores from asparagus.

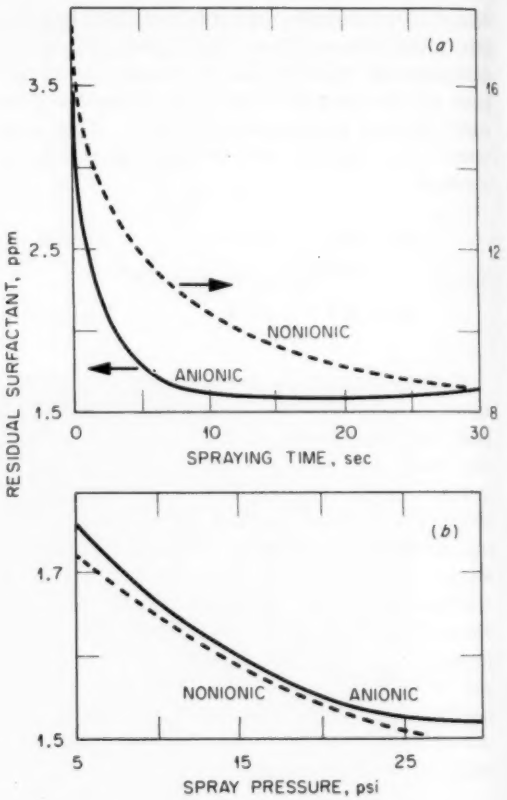


Fig. II-15 Effect of (*a*) time and (*b*) pressure of rinsing spray in removing surfactant anionic and nonionic residue from detergent-washed asparagus.

Pesticide Removal.[89] The Food Additives Amendment of the Federal Food, Drug, and Cosmetics Act states that a processed food shall "not be deemed unsafe if such residue in or on the raw agricultural commodity has been removed to the extent possible in good manufacturing practice, and the concentration of such residue in the processed food when ready to eat is not greater than the tolerances prescribed for the raw agricultural commodity." The extent to which detergents aid in removing pesticide residues is not known, nor has it been established to what extent residues are removed in the peeling, blanching, and other steps or what constitutes "good manufacturing practice." Commercial food-preparation procedures vary, and the effect of variations on residue removal has not been evaluated. Products that are concentrated during the manufacturing process, such as fruit and tomato concentrates, must conform to the same tolerances that apply to the raw agricultural commodity. Processors must aim at better residue removal but are faced at the same time with the necessity of conserving water and limiting liquid-waste discharges. There is therefore an urgent need for rapid, sensitive methods for routine determination of pesticide residues on foods undergoing commercial processing. Methods currently in use require extraction of the pesticide from the food and extensive purification of the extract prior to analysis. However, radiometric techniques may be used to determine both the residues at various stages of food processing and the efficiency of current analytical methods.

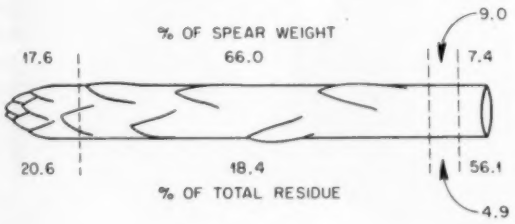


Fig. II-16 Distribution of detergent residue on washed and rinsed asparagus.

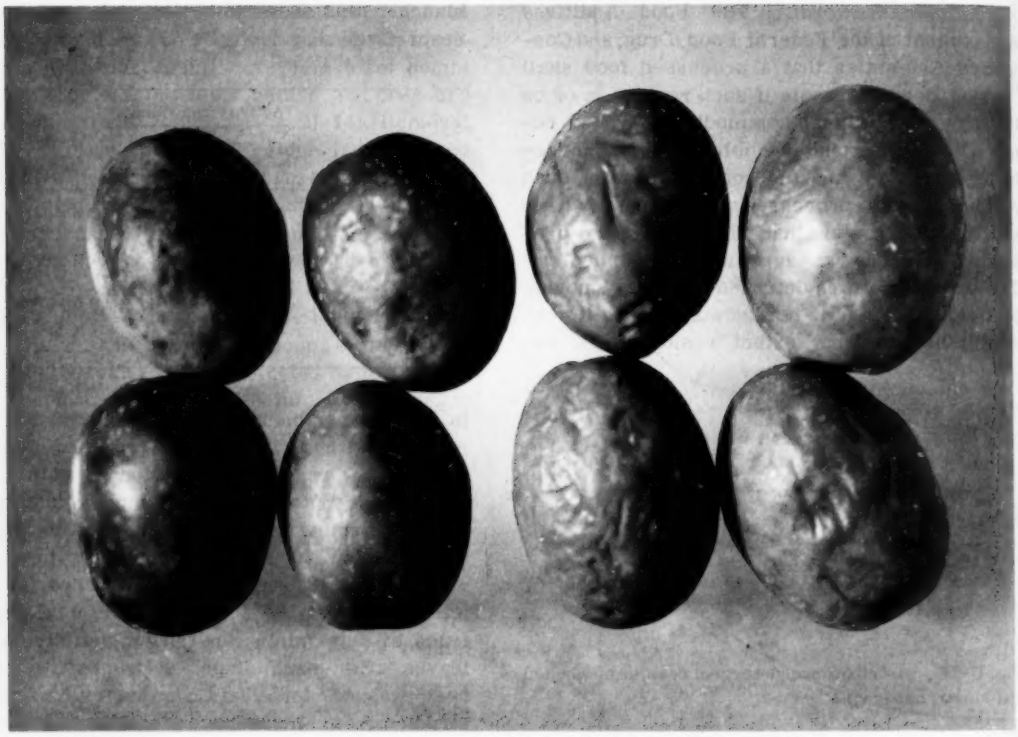
In studies on removal of pesticide from spinach in the washing and blanching steps, the difference in DDT-H^3 residue on unwashed spinach and spinach washed with detergent and blanched was shown to be only 4.4 and 2.4 ppm, respectively.

Treatment	Activity remaining: Counts/(min) (g of dry spinach)	Activity remaining: %	DDT on spinach, ppm
None	5860	100	4.4
Water washed	5120	87	3.8
Water washed and blanched	4440	76	3.3
Detergent washed	3690	63	2.8
Detergent washed and blanched	3260	56	2.4

In these experiments fresh market spinach was sprayed with a 1% DDT-H^3 (specific activity 0.63 μc/mg, page 246) emulsion in water at a rate designed to give a maximum residue of 7 ppm. The spinach leaves were detergent-washed at 80°F and 20 psi water pressure in a reel washer for 13 sec and then blanched for 2.5 min in water at 180°F. The residue levels were found by determining the tritium activity on the leaves after each stage of processing. This reel washer for leafy vegetables was constructed from an expanded stainless-steel drum set on wheels in an angle-iron frame, rotated by a Varidrive controlled motor. The reel can be elevated to an angle of 5° and has a spiral to facilitate movement of the product through the washer. In operation with products having radioactive residues, the entire unit is covered with polyethylene sheeting to confine any mist or spray.

In further tests spinach was grown in a laboratory chamber, harvested 21 days after application of DDT-H^3, and washed under maximum and minimum washing conditions with either detergent or fresh water. In each case the spinach received a flood wash, a fresh-water spray wash in the rotary-reel washer, and a hot-water blanch, with conditions varied to accomplish maximum removal of surface contaminants. The residue on the detergent-washed samples was lower than on the water-washed:

Washing conditions	Residual DDT, ppm	DDT removed, %
None	19.8	0
Water maximum	9.8	51
Detergent maximum	8.8	56
Water minimum	11.0	44
Detergent minimum	8.5	57



(*a*) (*b*)

Fig. II-17 Olives (*a*) washed and (*b*) not washed with detergent before being placed in brine.

Table II-10 CONCENTRATION OF DETERGENT RESIDUE IN OLIVES BEFORE AND AFTER SUCCESSIVE STAGES OF PROCESSING

Stage	Olives detergent-washed before storage in brine			Olives not washed, stored in brine with 100 ppm of detergent			Olives not washed, stored in brine with 1000 ppm of detergent		
	Radio-activity, counts/min	Concen-tration, ppm	% of orig-inal*	Radio-activity, counts/min	Concen-tration, ppm	% of orig-inal*	Radio-activity, counts/min	Concen-tration, ppm	% of orig-inal*
Before first lye treatment	21.3	2.0	100.0	39.3	3.7	100.0	370.6	35.2	100.0
After second lye treatment	17.0	1.6	79.8	30.2	2.9	77.0	336.8	32.0	90.9
After third lye treatment	11.7	1.1	54.9	23.8	2.3	60.6	313.4	29.8	84.5
After final lye treatment at elevated tem-perature	6.0	0.6	28.2	19.6	1.9	49.8	213.8	20.3	57.7
After final water rinse	6.2	0.6	29.1	16.7	1.6	42.5	217.1	20.6	58.6
After cooking 60 min at 240°F in 3% brine	4.8	0.5	22.6	8.8	0.8	22.4	146.7	13.9	39.6

*A value of 100% was assigned to that concentration of residue found before processing began.

The small discrepancy between the samples washed with detergent (maximum vs. minimum) was believed to result from variable plant growth and differences in pesticide-application conditions.

Evaluation of Current Analytical Methods. In a study of the efficiency of current methods of preparing food samples for analysis, DDT-C^{14} was added to tomato pomace and extracted by standard procedures. Contrary to general assumptions, multiple extractions with either acetonitrile or isopropanolhexane were required to recover more than 60% of the added pesticide (Fig. II-18). Acetonitrile was the better extractant. When this extract was purified by passage through an adsorbent column containing either Fluorisil or silica gel–alumina, recovery of the pesticide from the extract was high, and reproducibility of results was excellent (Fig. II-19).

Radioactive pesticides have been used to study previously unexplored variables in the fly bioassay method for pesticides. For example, the distribution of DDT-C^{14} in a bioassay was determined by measuring the radioactivity in the rinsings of the jar, jar cover, and food plug and the ashes of dead and live flies. That less than 10% of the material volatilized during the 24-hr test was shown by the greater than 90% recovery (Table II-11). Less than 10% of Aldrin-C^{14} was recovered under the same conditions.

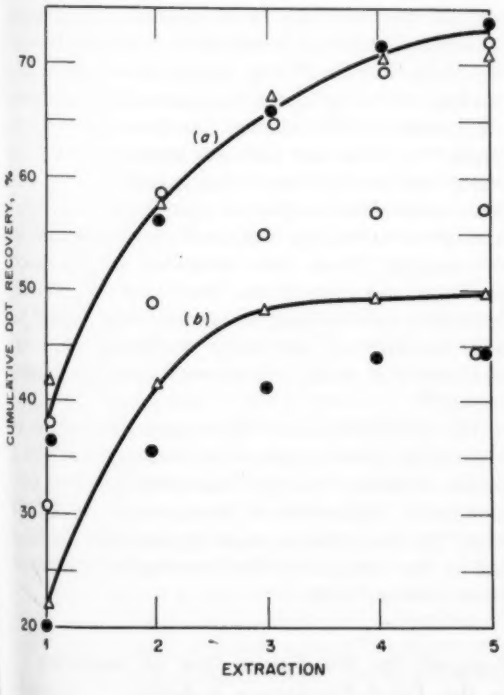


Fig. II-18 Recovery of DDT-C^{14} from tomato pomace by extraction with (*a*) acetonitrile and (*b*) isopropanolhexane.

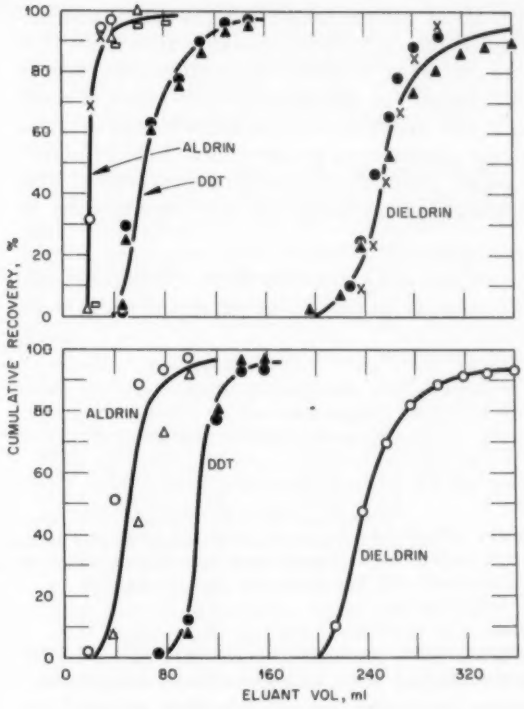


Fig. II-19 Recovery of Aldrin-C^{14}, DDT-C^{14}, and Dieldrin-C^{14}, added to tomato pomace extract, from (*a*) Fluorisil and (*b*) silica gel–alumina column cleanup.

Critical manipulations in the paper chromatographic analysis of pesticides were studied by radiochemical methods. A procedure was developed for simultaneous spotting of samples on paper prior to chromatographic separation (Table II-12), and excellent spots were formed with substantial saving of the time over the conventional micropipet spotting techniques.

Irradiation Sterilization of Canned Foods

Nontracer uses, for example, in radiation sterilization of food, are of less interest in the canning industry since the irradiation dose of

4.5 Mrad recommended for the safe sterilization of nonacid foods adversely affects the flavor of many of these foods. However, recent successes[90] in radiation pasteurization of meat and fish products will probably result in additional research on preservation of the principal canned products by radiation processing. The potential of radiation in cold sterilization of canned food captured the imagination of food scientists as soon as high-activity sources became available, and a definitive review[91] on this subject appeared in 1951.

Numerous workers had shown that the spore forms of fungi and bacteria are more resistant than vegetative forms to beta and gamma radiation, as they are also to heat. The most important spore-forming organism of interest to the canning industry from a public health standpoint is *Clostridium botulinum*, and it was necessary to establish the absolute or practical ability of gamma radiation to kill it. Early work in the National Canners Association laboratories[92] established that spores of this organism were more resistant to radiation than spores of other food-spoilage organisms, and conditions during spore production or irradiation had a marked effect on the radiation dose required for sterilization.

A collaborative project to determine the radiation dosage needed to produce sterility in five different canned foods was conducted by the National Canners Association, the American Can Company, and the Continental Can Company. With a mixture of fission products in spent fuel elements as the gamma-radiation source, *C. botulinum* was shown to be more resistant to radiation in foods than in neutral phosphate suspension when irradiated at freezing temperatures.[93] The resistance varied according to the product. In experimental packs containing 10,000 spores per gram, peas required 3.0 Mrad and pork 4.0 Mrad to give cans which did not produce toxic swells.[94] It was later shown that different strains of *C. botulinum* were strikingly different in resistance to irradiation. Since the character of the food partially determines the dose required for *C. botulinum* destruction, no single dose would be best for all food products.[95] Radiation survival curves for *C. botulinum* spores have been published.[96]

The combined effect of heat and radiation in sterilizing canned peas was investigated[97] in a major canning company laboratory. The organoleptic evaluation of peas processed by (1) heat, (2) irradiation, and (3) irradiation-heat led to the conclusion that thermally processed peas were superior.

Table II-11 DISTRIBUTION OF RADIOACTIVE DDT IN BIOASSAY JARS
(50 Flies per Jar; 3 Jars for Each Level of DDT; Jars Kept at 74°F for 24 Hr)

Dosage, μg per jar	Flies killed, %	DDT recovered,* μg						Amount recovered, %
		Jar	Jar cover	Food plug	Ashed flies†		Total	
					Dead	Live		
4.04	38	2.41	0.45	0.15	0.50	0.35	3.98	96.3
8.08	50	5.50	0.62	0.31	1.16	0.34	7.99	98.8
12.44	65	8.61	0.74	0.36	2.14	0.20	12.02	96.6

*Each result is average of three values.
†"Dead" flies were those killed by the pesticide; "live" flies survived the assay test but were killed later for analysis.

Table II-12 RETENTION OF RADIOACTIVE PESTICIDES ON PAPER CHROMATOGRAMS WITH VARIOUS SPOTTING CONDITIONS

Procedure	Pesticide retained, %		
	DDT-C^{14}	Aldrin-C^{14}	Dieldrin-C^{14}
Conventional			
Still air at 27°C	96.3–98.8		
(3 replicates)	(97.9)		
NCA modification			
Drying air at 50°C	82.3–99.9	86.8–105.0	83.4–99.5
(10 replicates)	(92.1)	(97.7)	(93.7)
Drying air at 70°C	54.2–75.7		
(5 replicates)	(66.8)		

Prospect for the Future Use of Isotopes in the Food-Processing Industry

The applications of isotopes in food-processing research and quality control cited in this

review demonstrate the imaginative way in which food scientists and technologists use isotopes to provide the public with wholesome and nutritious foods. However, the impressive collection of isotope uses represents only an introductory phase to a new era in food-processing research and quality control.

Increased food production, requirements for greater convenience in preparation and service of foods, and further automation of food-processing operations will demand increasingly sensitive and reliable methods for analysis and control. The demonstrated ability of isotope technology to contribute to the solution of research and production problems will cause an increased utilization of isotopes in food-processing operations in the future.

Radioactive Piston Rings for Evaluation of Engine Oils

Brugger, Rieke, and Semmler at the Laboratories for Applied Sciences, University of Chicago, recently reported[16] the results of a study on the use of a test engine with radioactive piston rings for the evaluation of engine oils. This work as originally conceived had two goals: (1) to develop radioactive piston rings for engine tests that had much lower radioactivity than the reactor-activated rings usually used[46] and (2) to develop a test using these radioactive rings for the routine evaluation of engine oils. Neither goal was completely achieved.

After unsuccessful attempts to use beta emitters (C^{14}, S^{35}, P^{32}, and Pm^{147}), these workers developed a technique for electroplating an inlay of nickel containing Co^{60} into a groove in an iron piston ring. These rings had only a few percent of the total gamma activity of reactor-activated rings; however, the problem of adherence of a heavy nickel plate in a small groove was difficult, and many of the attempts to plate inlays were unsuccessful.

The rate of piston-ring wear was measured with iron rings inlaid with an electrolytically deposited alloy of nickel and Co^{60}, with reactor-activated nickel-inlaid rings, and with reactor-activated iron rings. The tests were conducted with three types of engine oil in an air-cooled single-cylinder Briggs and Stratton model 23A engine. The concentration of radioactive debris transferred to the lubricant was monitored continuously with a scintillation detector. It was found qualitatively that the three types of rings rated the three oils similarly with respect to ring wear.

Although some useful results were obtained in this study, the authors felt that it was not an unqualified success. In their concluding remarks, they give their work the following candid evaluation, which contains much that would be valuable to anyone else planning work in this field:

> Insofar as the purpose of this work was to evaluate the feasibility of using nickel-radiocobalt rings in wear studies, we have succeeded, in a qualified way. In some special applications, the use of inlays may have value; however, pile-activated rings are not so dangerous to handle in practice and the complication of decay correction is minor.
>
> The value of wear studies in oil quality rating deserves a hard look; we were rather beguiled into oversimplifying the problem. The diversity of wear sites in an operating engine and the shifts in their relative and absolute importance as a function of operating and environmental conditions is at the core of any lubricant evaluation study. So far as piston ring wear studies per se have value, we believe that the pile-activated ring method has the most general value; any inlay, be it of nickel or of an active metal like zinc, or any coating like chromium, is bound to influence ring wear to a greater or lesser degree. There will, further, always be a need to adjust the radioactivity level of the wearing part to the type of study being made, in the interest of obtaining counting data which are statistically significant. For short-term studies with pile-activated rings, the health hazard might be major. One can make a case for the incorporation of a beta-emitter (like carbon-14 or promethium-147) into the cast iron with the expectation that the wearing properties of the iron would not be modified, but here the problem is one of development of a suitable method of detection. Activation analysis of debris-containing samples withdrawn from the crankcase has value in certain specific instances.
>
> Concerning some of the specific failings of ring wear studies in general and of our study in particular, one might separate the difficulties into those of procedure and those of equipment. There is no substitute for research-grade equipment. With our air cooled engine, we had no real control over operating temperatures, especially of the cylinder area. Our carburetor did not permit the fine adjustment which was desirable and our air filter had a questionable efficiency. Regulation and recording of engine speed and load were too qualitative. A problem of a different nature, and one which may not be always appreciated, has to do with crank-

case ventilation in test engines. A multi-cylinder engine has a constant crankcase volume—there is no air pumping. A single-cylinder unit tends to pump outside air into the crankcase, and the degree of mixing with the crankcase air depends to a great extent on the design of the breather tube. Insofar as extent of oxidation of lubricant and the quantity of volatiles held up is important in oil evaluations, the rather slight attention paid to crankcase gas composition by workers in the field is surprising; admittedly, the principal chemical alterations of the lubricant occur in the combustion area, with the products later being washed into the crankcase.

In the matter of procedures, there is the problem of obtaining representative samples of oil in any oil circulating method; one can make a strong case for withdrawal, counting, and return of lubricant samples. Settling out of wear debris and foaming of the oil are two problems which plagued us. We were remiss in not reconditioning the engine and in not carefully purging all oil circulating lines regularly, in not controlling piston ring finish and dimensions more rigorously, in failing to keep an accurate account of oil consumption, etc. In view of the shortcomings of our test engine, we feel that determination of lubricant viscosity and gravity changes, etc., would have been an unwarranted refinement. Finally, one must make a statistically significant number of runs so that differences between rings from different lots and lubricants from different batches—all of which satisfy the same applicable specifications, of course—can be knowledgeably interpreted.

One observation worth making—and one which we came to the hard way—is that any worthwhile study of wear and of lubricant quality in an internal combustion engine is a major undertaking: one cannot achieve much on a small scale or with inexpensive and makeshift equipment.

The authors prepared a comprehensive review of the literature on the general problem of engine wear; the use of tracer techniques for the evaluation of wear is reviewed in the following section.

Engine-Wear Studies with Radioisotopes

By J. E. Brugger, F. F. Rieke, and R. A. Semmler*

(Editor's Note: Comprehensive reviews of the literature of various facets of isotope uses will be carried in Isotopes and Radiation Technology *from time to time. This literature survey of the uses of radioisotope tracers in the study of engine wear was recently included as a part of the report[16] on the above work on engine wear. We are including it here with only slight modification since we believe it will be valuable to anyone working in this field.)*

In this literature survey the aim has been to review published material through 1961 on applications of radiotracers to piston-ring and cylinder-wear studies; however, certain citations have been included to publications on bearing-journal and cam-tappet wear in engines, on friction and wear studies of more general interest, on the formation, stability, and action of extreme-pressure-lubricant films, and on lubricant loss and consumption in engines since all these topics bear on the use of radioisotopes in engine tests for evaluation of oils.

Credit for showing the practical value of the radiochemical technique for following piston-ring wear is given to Ferris,[98] who performed the work at Battelle Memorial Institute in 1941 and obtained a patent (assigned to Atlantic Refining Company) on the use of cyclotron-produced P^{32} in ring-wear studies. He determined the radiophosphorus content, and hence wear-debris concentration, by counting aliquots of the lubricant.

In 1944 Sakmann, Burwell, and Irvine[99] reported on friction and wear studies of copper alloys that had been activated by deuteron bombardment. Both autoradiographic and G-M scanning techniques were used to follow the transfer of metal. In 1946 Gregory[100] of Australia used the autoradiographic method to follow the transfer of radiolead (obtained from spent radon tubes) from lead sliders to steel, copper, and lead plates.

In 1947 Sakmann, Grossman, and Irvine[101] labeled Nitralloy steel by incorporating cyclotron-produced Mn^{52} (from deuteron bombardment of chromium) into the melt. They dissolved the radioactive material transferred from a slider to a plate and determined it by counting. They were interested in studying the wearing rates for various pairs of surfaces commonly used in piston-ring and cylinder couples.

Burwell,[102] in an excellent account of the state of the art in 1947, discussed the four gen-

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eral radiotracer methods used in friction and wear studies: (1) surface activation by deuteron or proton bombardment; (2) electrodeposition of tagged material on a wearing surface; (3) addition of a radioisotope to the melt from which the metal samples are to be cast; and (4) reactor activation of metal parts. He reported on his own studies and reviewed theories of friction and wear and preparation and methods for determination of radiotracers.

In 1949 Pinotti, Hull, and McLaughlin[103] had piston rings activated in the ORNL graphite reactor and followed their wear in a single-cylinder diesel engine by periodically counting aliquots of oil. Ferris's patent, this study by Pinotti et al., and the work of Jackson and coworkers[104,105] in 1951–1952 provide the groundwork for all later ring-wear studies with radioisotopes.

In 1950 Burwell and Murray[106] installed Cr^{51}-plated rings in single-cylinder spark-ignition CFR* test engines and made an autoradiograph of the chromium transferred to and retained by the removable cylinder liner.

At the 1951 conference on radioisotope techniques at Oxford, Kerridge[107] reported on the use of radioisotopes in rather fundamental wear studies, which emphasized the importance of surface condition. Button, Davies, and Tourret[108] observed the wear of wire-drawing dies containing W^{187}.

In 1951 Burwell and Strang[109] reviewed their own work and that of others on the use of radioisotopes in friction and wear studies. Rabinowicz[110] and Rabinowicz and Tabor[111] reported on metal-transfer studies with autoradiography. An interesting experiment was one in which copper transfer to steel was demonstrated by briefly activating a steel specimen after the sliding had taken place; the intensely radioactive copper was clearly visible on autoradiographs. Other citations of early applications of radioisotopes in friction and wear studies are in the books of Bowden and Tabor[112] and in ASTM publications.[113–116]

Jackson et al.[104] reported on extensive radiotracer studies at a 1951 SAE meeting. Reactor-activated rings were installed in single-cylinder laboratory test engines, and wear was followed by counting of lubricant aliquots. The paper caused considerable interest in that it presented a documented case for the importance of low-temperature corrosive wear. In the discussion Savage mentioned studies of engine wear in production-line automobiles equipped with radioactive piston rings. In a later paper Jackson[105] presented evidence that single-cylinder laboratory engine radiotracer tests were valid in predicting the performance of wear-retarding oil compositions. In field trials the top-front compression rings of new and used automobiles were made radioactive, and the wear rates were determined by counting of oil aliquots. Borsoff and coworkers[117] used reactor-activated gears to study the effect of load and speed and of lubricant composition and temperature. Kavanagh[118] presented a correlation of wear predictions obtained with reactor-activated rings in standard test engines with the service performance data obtained from a taxicab fleet.

In 1953 Dyson and Williams[119] demonstrated the effectiveness of certain antiwear additives by counting aliquots of lubricant containing Fe^{59} from the top compression ring. Samples were taken every 2 hr, with running times of the order of hundreds of hours. They also proposed observing the wear of leaded copper bearings by following Tl^{204}, which forms a solid solution with lead, since available lead and copper isotopes were unsuitable. Popovich and Peterson[120] ran a related study on a diesel engine to check the effect of jacket temperature and fuel sulfur on ring wear. Hundere, Lawrason, and O'Meara[121] also used a diesel in their wear studies. They, as well as Miller and Jackson,[122] reviewed techniques commonly applied to reactor-activated ring studies and the radiation safety precautions to be followed.[123–125]

At the Second Oxford Radioisotopes Conference in 1954, Colding and Erwall[126] reported that it was possible to determine wear on both the rake and the clearance sides of carbide cutting tools by measuring the activity transferred to chips from W^{187}-containing tools.

At the Fourth World Petroleum Congress in Rome in June 1955, Fries, Hull, and Jones[127] discussed numerous applications of radioisotopes to petroleum technology, including lubricant antiwear action. Their bibliography includes almost a hundred citations.

During the July 1955 Moscow Conference of the USSR Academy of Sciences on the Peaceful Uses of Atomic Energy—a prelude to the United Nations Conference in Geneva in August—

*Cooperative Fuel Research, a joint program of the American Petroleum Institute and Society of Automotive Engineers.

Zaslavskii[128] reported on the use of reactor-activated piston rings in wear studies, as well as on the use of rings with Zn^{65}-containing pressed inserts and with Zn^{65} electrodeposited in an annular groove 0.2 mm deep by 0.25 mm wide. Nadeinskaya[129] discussed extensive tool-wear studies with W^{187}. In two 1955 publications Diachenko and Nisnevich[130] reported on ring-wear studies with radioisotopes, and Nisnevich and Shchurov[131] used radiotracers in an abrasive-wear study (see also Ref. 132). Godfrey[133] of California Research Corporation discussed the organization of Russian research on lubrication and wear, indicated sources of translated material, and summarized a dozen Russian papers on lubrication and wear studies published in 1956 or earlier.

At the First United Nations Conference on the Peaceful Uses of Atomic Energy in August 1955, Grozin[134] reviewed Russian studies on wear of machine parts. Hull and Fries[135] discussed studies of engine wear, deposit formation, and fuel combustion in their paper on radioisotope applications in the petroleum industry.

Hannum[136] installed reactor-activated rings, which had been plated with cold chromium, in a CFR engine and followed ring side-wear. He used an oil circulating system and a crystal scintillation detector (see also Ref. 137).

At the September 1956 ACS Meeting, Gorry[123] reported on studies with reactor-activated rings to evaluate detergent oils.

Merchant, Ernst, and Krabacher[138] reviewed applications of radiotracers in wear studies and specifically discussed their work on tool-wear measurement by counting W^{187} activity transferred to the chips.

A number of papers on applications of radioisotopes to friction, lubrication, and wear studies were presented at the April 1957 USSR All-Union Conference; many of them have been translated. Dikushin[139] summarized the uses of isotopes in "machine building," with emphasis on cutting-tool wear studies. Zamoruyev and Levin[140] tagged steel samples by incorporating P^{32} in the melt and labeled others by electroplating with Fe^{59}. The samples were carburized and heat-treated and then run against each other in a wear machine to determine the transfer of metal from one piece to the other. Their conclusions concerning the transfer mechanism were challenged by Vinogradov,[141] who also presented interesting observations on the action of sulfide layers as extreme-pressure agents and discussed the possible regeneration of the layer. Experimental studies on the action of the sulfide layer were made by Vainshtein and Vinogradov.[142] Kusakov[143] used S^{35}- and P^{32}-labeled lubricant additives to follow the reaction with metal surfaces as functions of surface temperature and of additive type (sulfides, disulfides, and alkylphosphites). Zaslavskii[144] paid special attention to the action of extreme-pressure additives on simulated lead-containing bearings. The formation and destruction of an anticorrosive layer was followed as a function of lubricant acidity. The work of Melik-Zade[145] was along similar lines but was less extensive. Zavelskii[146] undertook bench as well as engine-wear tests to follow the decreasing antiwear qualities of the oil as the organic impurities increased with engine operation. Radioactively labeled cast iron, both for wear-machine samples and for piston rings, was prepared by adding Co^{60} to the iron melt before casting. Stetsenko[147] also used cast iron containing Co^{60} in bench-scale studies of wear. Palatnik[148] studied the effect of the heat-treatment cycle on the structure and durability of case-hardened steel. The attrition of Cr^{51}- and Co^{60}-labeled samples was followed in a wear machine. Pavlov[149] followed the wear of a reactor-activated ball in a bench-scale wear test (modified four-ball apparatus). Nikitin[150] used Co^{60}-containing rings and installed reactor-activated plugs in the cylinder walls of a one-cylinder diesel for studying the effects of engine speed and cylinder pressure on engine wear. Zaslavskii[151] constructed a friction machine to simulate the action of the compression ring against the cylinder wall in an engine. Iron-59 was used as the wear tag. Sulfuric, formic, and acetic acid vapors were added to the lubricant (transformer oil). It is claimed that electrochemical corrosion is the chief factor causing wear in friction couples under these conditions. Nisnevich[132] tagged cast iron, bronze, and aluminum alloys with Fe^{59}, Zn^{65}, and Sb^{127} to follow their wear against steel in a bench-scale apparatus. Varying amounts of dirt and grit, such as occur on farms, were added to the oil. Also, engine tests were run with dust-containing oil. Compression rings were fitted with Zn^{65} inserts for these runs, which were designed to test the effectiveness of air filters used on farm tractor diesels. Vysotoskii[152] installed Zn^{65}-inlaid rings in the engines of some buses and Co^{60}-

tagged rings in others. The vehicles were equipped with oil-circulating and counting equipment and with devices for monitoring the dirt content of the intake air. Data on ring wear were reported for trips totaling 4000 miles. Studnits[153] inserted Zn^{65} plugs in the teeth of pinion gears to follow face wear. Lazebnik[154] attempted to derive formulas for predicting the wear rate of cutting tools, based on data obtained from radiotracer tool-wear studies. Yakovlev[155] used an autoradiographic method to follow tool wear as a function of cutting speed and surface finish. Kazakov[156] used W^{187} and Co^{60} as tags to follow tool wear both autoradiographically and by determining the activity of the collected chips. Yudin[157] used nickel-Co^{60} inserts to follow fuel-pump-bearing wear.

At the June 1957 Pittsburgh Meeting of the American Nuclear Society, Gumbleton et al.[158,159] presented a series of papers on piston-ring wear with Fe^{59}. The General Motors Institute operates a "Radioisotopes in Industry Training Program."[115,160,161] The study guides[160] include instructions for running ring-wear tests.

At the Institution of Mechanical Engineers Conference on Lubrication and Wear in London in October 1957, a number of papers on applications of radioisotopes were presented; summaries are included in the review papers of Barwell,[162] Christopherson,[163] Davies,[164] and Withers.[165] Specifically, Grunberg and Campbell[166] used an autoradiographic technique to follow the transfer of copper onto steel; Lancaster[167] followed the buildup of films of softer metals on harder ones; Edgar[168] designed a unique cylinder-wall oil sampler to follow the wear of reactor-activated piston rings; Merchant[169] made autoradiographs of chip samples to determine the relative sizes of tool-wear particles; Campbell[170] used S^{35}-containing lubricants to study the formation and stability of sulfide films under boundary conditions, showing autoradiographically that the film extended beyond the region of intimate contact in a crossed-cylinder machine; Palmgren and Snare[171] used radioisotopic tracing in a bearing study.

At the UNESCO Conference on Radioisotopes in Research, Paris, September 1957, Golden and Rowe[172] outlined their use of scintillation counting and autoradiography to follow the transfer of W^{187} from tungsten carbide sliders to copper-plated disks. Palatnik et al.[173] reported that the wear resistance of case-hardened steel is determined by its "fine structure." They followed the wear of various hardened gears by monitoring the Fe^{59} transferred to the grease.

Also in 1957 Landergren[174] followed the wear of reactor-activated ball bearings by periodically separating the Fe^{59} chemically from the grease and determining its activity. Burwell[175] at MIT studied metal transfer using both cyclotron- and reactor-produced isotopes and counting and autoradiographic techniques. Campbell and Harriden[176] studied the boundary lubrication provided by paraffinics and by oleic acid-containing lubricants for Cu^{64} sliders moving on steel plates. Snow and Skonecke[124] used a circulating system and scintillation detector to follow wear of reactor-activated piston rings in a cooperative oil test (COT) engine. They also followed cutting-tool wear and evaluated cutting oils by means of Ta^{182} transferred from the tool to the chips, the chips being collected and counted. Savage and Bowman[177] tagged lead-base Babbitt connecting-rod bearings with Sb^{124} and followed wear of the bearing by monitoring the Sb^{124} transferred to the oil. High wear rates were observed during startup and during high-speed operation. SAE 10W oil occasioned high wear rates when used at normal operating temperatures. Flom[178] used counting and autoradiographic methods to follow the transfer of radiosilver-labeled silver and silver-graphite riders to graphite and to copper cylinders. Back transfer from cylinder to the rider was also studied.

In 1958 Batzold, Clarke, and Kunc[179] followed the wear of the piston rings of a car in actual service. Reactor-activated compression rings were installed, and the wear was continuously monitored by an air-cooled scintillation detector. Agius and Pegg[180] installed reactor-activated cylinder liners in car and truck engines. Oil samples were periodically withdrawn and counted in the laboratory.

Kohn[181] published a survey of the applications of isotopes to friction and wear studies. As part of a series on radioisotopes in industry, Allen[182] and Smith[183] reviewed applications to wear of machine parts including piston rings, gears, bearings, cutting tools, and even drop-forge hammers.

Pontious[184] installed a reactor-activated compression ring in a cooperative oil test engine and used a scintillation detector to monitor continuously the activity transferred to the oil. The lubricant was cooled before passing through the counting chamber and reheated before its

return to the crankcase. Runs were made for normal, as well as for low-temperature stop-and-go, operations.

Abowd[137,185] pioneered the technique of using Cr^{51} face-plated, reactor-activated compression rings to follow ring face and side wear simultaneously. Using a scintillation detector in an oil circulating system, he demonstrated that the distribution of ring wear between ring face and side depends on oil composition and that, during continual preignition, top compression rings show extremely great adhesive (frictional) wear, which could be reduced by addition of extreme-pressure agents to the lubricant. It was shown that oil compositions satisfactory for plain cast-iron rings may be unsuitable for use with chrome-plated rings.

Okrent and Weisgerber[186] installed reactor-activated hardenable cast-iron valve lifters in a V-8 engine. Lubricant samples were withdrawn regularly for counting, and the 1.1-Mev Fe^{59} photopeak was monitored.

Shore and Ockert[187] used C^{14}-tagged fuel components to follow the effect of gasoline composition on combustion-chamber deposit formation. High-boiling components and aromatics showed strong deposit-formation tendencies, confirming previous studies. Cooper, Courtney, and Hall[188] also used C^{14}-tagged fuels and followed the distribution of CO_2, CO, partially oxidized fuel, and unburned fuel in the exhaust and crankcase gases as functions of engine operating conditions. In certain instances they observed a fractionation of fuel in the intake manifold, resulting in a maldistribution of high- and low-boiling components in the cylinders. Guinn and Coit[189] followed the consumption of tritium-labeled oil by collecting water-vapor samples (containing THO) from the exhaust and blow-by gases and determining the activity by liquid scintillation counting. Fries, Davis, and Hull[190] made engine airflow measurements with Kr^{85} in the air and Hull's total count method.

Loeser, Wiquist, and Twiss[191–193] followed the formation and breakdown of extreme-pressure films on cam and tappet surfaces by determining surface activity and distribution of tagged oils and additives. In dynamic testing of zinc dithiophosphates, the zinc and phosphorus contents of the film increased more rapidly than the sulfur content with increased operating pressures and temperatures. Once laid down, the films were quite stable even during running with additive-free lubricants. Furey's work[194] also supports the thesis of protective film formation by chemical action in regions of greatest stress, surface damage, and metal transfer.

Although fuel and lubricant tagging with H^3, C^{14}, P^{32}, and S^{35} are widely used and contribute in some degree to our understanding of ring-cylinder wear, it is beyond the scope of this report to expand on this interesting application of tracers.[127,194]

At the Second Japan Conference on the Uses of Radioisotopes, February 1958, Sata[195] reported on the mechanism of metal wear of a Zn^{65}-plated steel slider on a carburized steel plate that had been given a surface roughness of 3.5 to 7 μ with emery cloth. The distribution in number and size of wear particles transferred to the steel was determined autoradiographically and by projection microscopy. Kato[196] reported on isotopes from 15-Mev deuteron bombardment of cast-iron piston rings for wear studies (gamma energies in Mev and half-lives are given in parentheses): Mn^{54} (0.84, 324 days); Co^{56} (0.85 and others, 80 days); Co^{57} (0.12, 270 days); Co^{58} (0.81, 72 days); P^{32} (1.70 β, 14 days); Fe^{55} (0.21 EC, 3.0, 2.7 years). The energy composition of the radiation and the beta/gamma ratio changed, of course, with time. For short times, it was preferable to monitor the beta activity and, after long times, the gamma radiations (approximately 0.85 Mev) from the several species. Difficulties were experienced in correlating wear with counts detected because of the thinness of the activated layer and its geometric and isotopic inhomogeneities.

At the Second United Nations International Conference on the Peaceful Uses of Atomic Energy in September 1958, Spinks[197] reported on the use of reactor-activated piston rings in the single-cylinder Lauson test engine. Preliminary evaluations of various lubricants were undertaken. Topchiev, Aladiev, and Savitsky[198] reviewed Russian work on the action of extreme-pressure additives and on corrosion inhibitors. He also surveyed newer developments in industrial uses reported to the Conference.[199] Erwall[200] outlined methods for diffusing radioisotopes into the surface layers of parts too large to be activated in a reactor. Schultz et al.[201] discussed the measurement of gear wear by activation analysis for Mn^{56} in the lubricant. Deterding and Calow[202] reported successful monitoring of the wear of reactor-activated top compression rings in two cylinders

of the engine of a moving vehicle. The Fe^{59} activity transferred to the oil was monitored continuously with an air-cooled scintillation crystal and a strip-chart recorder. The effect of speed and of various antiwear additives on ring wear rate was clearly shown. Zaslavskii, Shor, and Shneyerova[203] used various isotopes in studying the antiwear films formed by certain sulfur- and phosphorus-containing additives and in determining the effectiveness of additives in combating corrosive wear. Pavelescu and Iliuc[204] irradiated lubricants in a reactor to generate intrinsic S^{35} and P^{32} tags. By determining the specific activity of lubricant films under conditions of hydrodynamic lubrication, they were able to determine film thickness as a function of viscosity for specified conditions.

At the Fifth World Petroleum Congress in 1959, Furey and Kunc[205] discussed the uses of radioisotopes in fuel and lubricant research, with citation of 102 references. An extensive bibliography of the uses of radioisotopes is published in Volume 2 of *Progress in Non-Destructive Testing*,[206] and the monograph of Rochlin and Schultz[207] on industrial uses of radioisotopes includes references. In passing, it might be added that references to wear studies appear regularly in the journal *Wear* as part of the "Systematic Abstracts" section prepared by Battelle Memorial Institute (see Ref. 208, for example).

At the Third Japan Conference[209] on Radioisotopes in 1959, Kato[210] reported on reactor-activated ring studies and emphasized the need for paying close attention to iron balance, to the problems of uniform distribution of wear particles in the oil, and to the prevention of the settling out of wear debris. Sakurai[211] discussed the formation of iron sulfide on surfaces by the action of S^{35}-containing extreme-pressure-lubricant additives. Sata and Nakajima[212] studied the wear of tool bits in terms of W^{187} transferred to the chips. The carbide tool tips were reactor activated.

Briggs and Coultry[213] studied gear wear by an activation technique. Samples of the lubricant were irradiated, and the activity of the Mn^{56} from the wear debris was used as the measure of wear. Because of the variable amount of aluminum in compounded greases, Al^{28} activity was not a suitable monitor. Aluminum-28 could be used as the tag when silicon was absent since Al^{28} was formed both by a fast-neutron (n,p) reaction on Si^{28} and by the slow-neutron (n,γ) reaction on Al^{27}.

Evans and Landen[214] reported on a number of tracer studies. One of interest involved the surface uptake of P^{32} by cast iron. Bushing "bleeding" tests were conducted with Zn^{65}. Cesium-134 was used to trace coolant leaks, and bearing seizure studies were also made with reactor-activated Fe^{59}-containing components.

In an interesting application of radioisotopes, Testerman[215] used I^{131} to determine the surface roughness of gold (standard), brass, and aluminum samples.

Thiery[216] installed gutters at the bottom of the cylinder to collect oil that drained from the exterior of the piston. A reactor-activated ring was used. He monitored the activity in the oil as it moved down the side of the piston as well as that of the oil in the crankcase. The method emphasizes changes in wear rate.

Jursch, Pinotti, and Jones[217] used reactor-activated rings to study wear in railroad diesels. Counting with G-M tubes was done aboard the locomotive.

Crook[218] summarized extensive studies on wear and lubrication, in which considerable use was made of radioisotope techniques.

In September 1960 UNESCO and the International Atomic Energy Agency cosponsored the Conference on the Use of Radioisotopes in the Physical Sciences and Industry at Copenhagen. Howes, Braun, and Sunderman[219] reported on cylinder-liner wear in a 1000-hp diesel. They also followed lubricating-oil consumption as a function of break-in time, engine speed, and engine load by monitoring exhaust gas. A high-detergency oil was tagged by adding a Zn^{65} phosphate ester. Losses of oil or tracer by vaporization and settling out were prevented or accounted for. Campbell et al.[220] installed small reactor-activated iridium-containing cast-iron plugs at various levels and positions on the walls of a diesel cylinder liner. The trace (0.03%) of iridium was added to the cast iron "to increase the sensitivity of the method." Aliquots of the lubricant were removed and counted. They propose to modify the method for simultaneously following the wear at different areas of the liner through multiple tagging and pulse-height analysis. Ferric oxide was shown to be more abrasive than Fe_3O_4 through autoradiographic studies of metal plates that had been subjected to abrasive wear by the

reactor-activated iron oxides. Buildup times for S^{35}- and P^{32}-tagged antiwear additives were investigated as functions of load, speed, and running time for automotive gears. Zaslavskii and Shor[221] reported on the use of tagged carbon black in soot sedimentation studies, on radiocopper tracer studies to aid in compounding bearing lubricants having maximized antiwear qualities and minimal corrosive action, and on beta-ray thickness gaging of engine varnishes to evaluate the detergent action of engine oils. Frynta, Kkhol, and Kopetskii[222] claim to have followed the wear of a bearing containing radiosilver for over 3600 hr operation by monitoring the activity remaining in the bearing. Sata, Abe, and Nakajima[223] showed that wear of a die can be found from activity transferred to the disks cut out and the wear of the punch from the radioactivity of the edges of the holes. Wear rates, which differ for punch and die, were measured with various extreme-pressure-containing lubricants and for different metals.

Arnold et al.[224] irradiated a section of a 160-lb 42-in.-long 8-in.-bore cylinder liner for an opposed-piston diesel in a pool reactor. The level of activity of the liner was very high; but, by proper scheduling of work periods of personnel, it was possible to hold dose limits within legal requirements. Further, because the liner was not uniformly irradiated, the activity profile of the liner changed with time. Activity arose from Fe^{59}, Cr^{51}, and Mn^{54}. Arnold describes the method by which the liner was shielded, encapsulated, and manipulated in the reactor. Aliquot sampling was used on the lubricating oil; the exhaust gas and engine deposits were also monitored. In this work 80% of the wear debris was found in the oil, 5% in deposits and 10% in the exhaust and 5% was unaccounted for. The method of computing total wear is not specified. The work was discussed by Gumbleton.[225]

Jaspert and Reuter[226] discussed the advantages of radiotracing as compared to spectrochemical analysis in engine-wear studies.

Halliwell[227] followed the face (Cr^{51}) and the side and back (Fe^{59}) wear of chrome-plated rings in a General Motors-71 diesel (see also Ref. 137) in a study of filtration of oils with a high level of detergency. The special interest was in determining to what extent detergent oils might entrain and hold fine abrasives (from dirty fuel) and in evaluating full- and partial-flow oil filters.

Chromium and iron tracing, as well as gravimetric checking, was applied by Robbins, Pinotti, and Jones[228] to study the wear effects of engine speed and load, jacket water temperature, fuel temperature, and chrome plating of rings in a medium-speed diesel operated on distillate and on residual fuels. They accounted for 85% of the wear debris through radioactivity measurements, the total wear being determined by weighing. The loss of lubricant through leakage and as engine exhaust has been specifically studied by several investigators.[189,229] Unaccounted-for lubricant and debris loss can influence radioactivity-based wear data interpretation.

At the Fourth Japan Conference[230] on Radioisotopes in October 1961, Wada and Maeda[231] reported on the preparation of Cr^{51}-plated top compression rings for use in a diesel-engine wear study. Tamura et al.[232] studied the wear rate of reactor-activated (Fe^{59}) punches and dies in a blanking operation. For 5-mm strips the relative wear rates for silicon steel, carbon steel, copper, and aluminum were approximately 100, 20, 2.5, and 1, respectively.

Kazlauskas, Ferris, and Herfurth[233] installed reactor-activated rings in delivery vehicles and evaluated the effect of airflow (excessive air cooling) on engine wear. Wear was low when the inlet coolant temperature was maintained at 160 to 170°F by using both line thermostats and air-shutter controls. Martin and Williams[234] followed both chrome-face and iron-side wear of railroad diesel compression and oil control rings as functions of injector design and of fuel type and quality.

Pinotti and coworkers[235] recently applied the reactor-activated compression-ring method for evaluating engine and lubricant performance to 16-cylinder railroad diesels and to a 6000-hp marine diesel, both in actual use studies. Price et al.[236] ran similar studies in highway construction diesels.

Of particular interest in connection with reactor-activated piston-ring-wear studies is Gumbleton's discussion[237] of their potentials and limitations. Reference is also made to the book by Kohl, Zentner, and Lukens.[238]

The following foreign-language literature was reviewed from abstracts published by the AEC Divisions of Isotopes Development and Technical Information.[239–243] These abstracts are prepared by the Science and Technology Division of the Library of Congress for the AEC

and distributed by the Library of Congress on 3 by 5 cards, which are assigned consecutive OID numbers.

In 1958 Wilputte[244] replaced a standard-size piston ring with a reactor-activated segment and followed its wear in an engine by determining the activity transferred to the oil. Surprisingly, he reported that engine temperature had little influence on wear. Stoll[245] used reactor-activated rings, G-M tubes, and aliquot sampling in his engine-wear study. Golov[246] gives the specifics of the Russian method for forming a radiozinc inlay in the face of a piston ring.[128,134] Propstl[247] installed Co^{60}-tagged cast-iron rings in the engine of a motor car and counted aliquots of the lubricant to determine engine wear under actual operating conditions. Tarasendo[248] used Ag^{110} in metal-cutting studies. Colding[249] determined the cutting-wear rate of radioactive carbide tools with both thin- and heavy-wall G-M tubes. Smorodinov[250] used W^{187}-containing tools in a study of cutter wear in stone quarrying. Arkuszewski[251] and Broda[252] reviewed applications of radioisotopes in machine-wear studies. Nisnevich[253] reported on the use of a scintillation detector for following attrition of radioactive machine parts. Tochilnikov[254] discussed the surface activity attainable by reactor activation, electroplating, and implantation of inserts in machine parts and gave formulas for computing the time required to attain a given specific activity of Fe^{59} in reactor-activated samples. Haga and Nagada[255,256] reported on wear machine evaluations of the lubricating qualities of various aromatic compounds. In one study, Sr^{90} transferred from a slider to a metal plate was followed autoradiographically; in the other, radiosilver lost from the slider was monitored with a G-M tube.

In 1959 Gerwin[257] reported on the Bosch Company (Stuttgart) "atomic automobile." A reactor-activated piston ring (containing 1% cobalt) was installed in a car, and accumulation of Co^{60} and Fe^{59} in the oil and uptake by the oil filter were determined periodically. Magarik and Nikolskii[258] used a scintillation detector to determine the quantities of Fe^{59} and Cr^{51} transferred from a piston ring to aliquots of lubricant. Smorodinov[259] followed the wear of reactor-activated rock cutting tools (W^{187}). Hsiung[260] studied the wear of radiocobalt-containing cutting tools.

In 1960 Nisnevich[261] piped the oil from a diesel having a reactor-activated ring through a water-cooled scintillation-detector assembly and followed the wear continuously (see also Ref. 253). Pavelescu[262] used G-M tubes in the lubricant supply line to follow the wear of reactor-activated bearings. Lachmann,[263] Fodor,[264] Nisnevich,[265] Rumiantsev,[266] and Daudel[267] reviewed the techniques for making wear studies, the criteria governing the choice of isotopes, and the advantages of the several methods of tagging. Sata et al.[268] studied the wear of reactor-activated punch and die sets. Among other observations, wear was shown to decrease with decreasing tool clearance (see also Ref. 223). Fujii and Hirano[269] used reactor-activated carbide tools to show the marked effect of both the method of lubrication and type of lubricant at higher cutting speeds. Nadeinskaia[270] used beta emitters in work on the wear of face milling cutters. Popov,[271] compared a two-tool method of Nadeinskaia with the commonly used one-tool method. In the two-tool system, the activity transferred to the working piece by a radioactive tool is removed by a following inactive tool. Kazakov[272] wrote a 327-page book, with 236 references, on the use of radioisotopes in investigating cutting-tool wear.

In 1961 Kaspar-Sickermann[273] reviewed the various procedures in use for following piston-ring wear. He covered the choice of isotope, measuring methods, and overall advantages. Monnot, Pons, and Thiery[274] applied a radiotracer method to the study of the wear of diesel-fuel injector parts. Pavelescu, Iliuc, and Barbul[275] continued their studies on the evaluation of additive oils in friction machines (see also Ref. 262). Zinc-65, Ag^{110}, and In^{114} were used as tags. Lapatukhin and Ovchinnikov[276] determined the variation of concentration with depth of penetration of P^{32}-labeled phosphoric acid used as a surface phosphatizing agent. Liu[277] reviewed Chinese work on isotope-based tool-wear studies. Turek and Cesanek[278] followed the total wear of the cutting tip of a W^{187}-tagged tool. Kieszniewski et al.[279] followed the wear of reactor-activated wire-drawing dies (sintered, with 6% cobalt) as a function of wire size, drawing speed, and lubricant composition. Ramdohr[280] installed Cr^{51}- and Fe^{59}-containing ball bearings in the fast-turning spindle drives of textile machines and demonstrated the great advantage of replacing the lubricant after a short run-in time for new parts. Break-in wear debris caused excessive wear. At the 1961

Krakow Conference, Michalowska[281] reported on laboratory and engine evaluations, made with Fe^{59}, Co^{60}, and Zn^{65}, of the "oiliness" of mineral oils. Pradzynski and Wajnsztejn[282] added reactor-activated ferrosilicon grit to bearing lubricants and followed the uptake of the grit by the bearing material. Banasik[283] used a scintillation detector to follow activity transferred to the lubricant in an "Amsler" wear-testing machine.

In 1962 Horiguchi and Okawa[284] used a scintillation detector to follow the wear of Cu^{64}, Sb^{124}-Cu^{64} alloy, and Cr^{51}-plated steel samples. Saitoh[285] used various isotopes to follow the buildup of precombustion deposits in automotive diesels. Pavelescu and Iliuc[286] incorporated In^{114} as an oil-soluble organometallic in bearing lubricants and attempted to determine the film thickness from the total activity of the lubricant held by a bearing journal, but data were erratic. Kollmann and Stegemann,[287] Oswald,[288] and Filip[289] each reviewed applications of radioactive parts to piston-ring and machine wear studies. Kollmann also discussed the use of Ag^{110m} implants to follow piston-ring rotation and the use of beta emitters, especially P^{32}, in lubricant film-thickness measurements.

Use of Radioisotopes in the Foreign Coal Industry

By George J. Rotariu*

The applications of radioisotopes in the foreign coal industry, as reported in the literature from 1958 to mid-1963, are reviewed here; two earlier reviews[290] on this subject are devoted largely to domestic work. The intense competition with hydroelectric power in some countries and soon with nuclear energy, together with steadily increasing labor costs, has led to rapid mechanization and automation of the coal industry, and radioisotopes provide unique and economical means of continuous, rapid, and automatic analysis, regulation, and control.

Although the U. S. coal industry has been experiencing a decline, e.g., from 520 million net tons in 1957 to 420 million net tons in 1961, very recent analyses[291] indicate that the bottom has been reached and that gradual annual increases are to be expected due to growth in electric power needs. The 1962 production was 422 million tons, and 769 million tons is predicted for 1975. Both the USSR and Communist China, who increased their production from 410 to 520 and from 144 to 420 million net tons, respectively, over the period 1957 to 1961, are reported to be using numerous radioisotope devices for control, automation, and analysis. The medium-range coal producers—the United Kingdom, West Germany, and Poland—and the smaller but technically more advanced coal producers—France, Belgium, the Netherlands, Italy, East Germany, Czechoslovakia, Austria, Hungary, Yugoslavia, and particularly Japan—are reportedly incorporating radioisotopic methods and devices into coal production. Many of these methods and devices are adaptations of American, Russian, and West German developments and are related to research being done under AEC Division of Isotopes Development (DID) contracts. For example, a technique using Kr^{85} clathrates was developed under DID sponsorship for continuously measuring SO_2 in the atmosphere in concentrations of parts per million [*Isotopes and Radiation Technology*, 1(1): 59], and research should be encouraged to determine how this might be applied in mine safety measures. Much effort is being sponsored on application of the neutron activation technique, and there is interest in New York Central's development of fast, automatic weighing of coal in train cars while the train is moving at high speed. The tagging of explosives which may be used in mining with gamma emitters such as Co^{60}, so that nonexploded charges may be found and accidents prevented, has been investigated in the United States.

Radioisotopes have been used in all phases of the coal industry: prospecting for coal seams; detecting noxious gases in underground mines; loading coal into carts or on belts for carrying to the surface and into surface conveyors for carrying to the processing plant; removing shale and other unwanted materials; washing, drying, grading, and blending for a particular use; and loading into conveyors for transportation to the consumer.

Two significant publications in this field are a Russian[292] one in 1961, *The Use of Radioisotopes for Automation in the Coal Industry*, and a two-volume Japanese[293] one, *Utilization and Ap-*

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plication of Radioisotopes in Mining. The Russian publication is outstanding and covers such items as the general problems of applying radioisotopes to the coal industry plus automation and control applications. Parts 1 to 3 of the Japanese publication emphasize fundamentals of radioisotopic techniques; Parts 4 to 6 cover industrial applications.

Exploration and Prospecting

For strip or open-pit mining, groundwater must be completely drained. In hydrogeological exploration in West Germany, 36-hr Br^{82} as NH_4Br or 8-day I^{131} as NaI, in very dilute water solution, is injected into the borehole, and at regular intervals the attenuation due to the mixing of the radioactive water with the surrounding water is measured.[294] In Soviet Russia groundwater movement is measured, and natural moisture content, soil density, and soil erosion are determined with radioisotopes.[295] In a Russian adaptation[296] of American oil-prospecting techniques to the study of rock formation and coal seams, one or more specially constructed steel bullets containing Co^{60} are shot into the strata, and the 1.2-Mev gamma radiation is measured at the surface. Tests made in 1957 in the Karenganda coal region down to depths of 150 m indicated the device to be satisfactory.

"Gamma-gamma logging," another new method now widely used in the USSR to define coal-bearing strata to distinguish them from overlying and underlying layers, was developed[297] for use in locating the Urals' coal deposits. A Co^{60} source and detector are lowered into boreholes, and the gamma-ray scattering distribution is measured. In the case of complex strata, two or more Geiger counters at different distances from the same source are used. It was shown that this gamma-gamma method yielded more valuable results on coal beds than the neutron-gamma logging technique. Other gamma sources used[298] for radioactive core sampling include Se^{75}, a 120-day-half-life soft-gamma emitter, and Sb^{124}, a 60-day-half-life stronger gamma emitter. This technique is particularly valuable for exploring coal beds where the electrical resistivity is low (as for brown coal) and thus a resistivity method is impractical.

Mining Operations

A sensitive gamma-radiation gage, with a Co^{60} source, for automatic control of the minimum and maximum coal levels in hydraulic mining operations is reported from Communist China.[299]

A method using the difference in gamma-radiation dispersion by coal and rock for automatic control of the shaft-sinking machine has been proposed in the USSR.[300] Preliminary experiments indicated it to be feasible. In 1960, at a conference on the introduction of radioisotopes and nuclear radiation into the national economy, papers were given on development of special instruments and their application in the mining industry; and gamma-relay devices for controlling automated loading of charging skips and of jaw-crusher mouths, controlling coal on conveyor belts, and accounting for carts being unloaded were described.[301]

The instrument-development effort in the USSR appears to be well coordinated with the applications needs. At the Riga Conference[302] in 1957, a counter and a gamma relay were described for automation of production processes in mines, at concentration mills, and in open-pit coal mines. Both induced activity and scattered radiation from radioactive isotopes were reported[303] for stabilization of mining and shaft-sinking machines, separating rock and coal, determining slurry densities, measuring the methane content of air, and determining rock and coal levels.

Nieman in 1959 discussed Russian methods for producing radioisotopes, their properties, and applicability for industrial purposes, including the automation and control of mining works, plus coal prospecting.[304]

Safety during mining operations is increased by testing the effectiveness of dust exhaust apparatus with finely powdered rubidium platinum chloride labeled with Rb^{85}, which has physical properties similar to those of the dust in coal mines. The efficiency of air exchange in mines has been studied with Br^{82}-labeled methyl bromide, and experiments are under way in West Germany on the use of other radioactive materials as methane indicators.[305]

The 18.7-day beta-gamma emitter Rb^{86} can be used in underground mining operations to trace the seepage path of underground water and prevent possible flooding hazards.[305]

Processing

The Moscow Mining Institute has developed a gamma-location method for studying the jigging

process.[306] Coal particles tagged with radioactive isotopes emitting hard gammas are tracked three-dimensionally with a system of counters, and the time-motion of the particles is recorded continuously for each coordinate. In a comprehensive study on the use of gamma-ray attenuation for separating coal from rock or pyrites,[307] the difference in attenuation (contrast) was shown to increase with decreasing gamma-ray energy from 1.3 to 0.085 Mev, increasing thickness of absorbing layer, and increasing pyrite content. In a detailed study on the applicability of radiometric systems for separating rock from useful minerals,[308] a gamma-absorption system was used to control separation of rock from coal in chutes. Curves were prepared which show the difference in gamma absorption of coal and rock as a function of their linear dimensions and the dependence of the absorption coefficient of radiation on the energy. Studies on neutron-activation techniques for rock-coal separation[309] showed that Al^{27} can be used to distinguish rock from coal. Plots of activity induced in samples of rock and coal, in both powder and lump form, by neutron irradiation vs. aluminum content indicated the absence of any masking effect by other elements present. A cascade sampling system was used to avoid having to scan the total mine output. A gamma-relay device is used for scanning and sorting the mined material.

From East Germany is reported[310] a process for determining the rate of coal movement through rotary kiln driers by measuring the radiation from introduced beta-gamma emitters. The coal is labeled by impregnating a small batch of coal particles with solutions of sodium or gold salts, activating this in a nuclear reactor, and mixing the resulting radioisotope-labeled coal particles with the coal to be dried. As the labeled coal moves through the kiln, the Na^{24} and Au^{198} formed by the activation are detected by special techniques to avoid interference by other induced radionuclides, e.g., S^{35}, Mg^{24}, and C^{14}. Gold is preferable to sodium because of the longer half-life of the activated product (Au^{108}, 2.7 days, and Na^{24}, 15 hr).

The USSR has used two pure-beta emitters, S^{35} (87 days) and P^{32} (14.3 days), for measuring[311] mixing efficiency during blending. Neutron-activated coal is added to the coal batch before the mixing operation, and during mixing the radiation is plotted against the weight of the coal batch and the percentage of activated coal.

In order to improve the quality of coke to meet the ever-increasing metallurgical requirements, the coking process was studied[312] with Kutznetsk coals from the Korov mine in Soviet Russia. The plastic deformation in autoradiographs of coke samples containing the pure-beta emitter Ca^{45} (165 days), added as $CaCl_2$ to the raw coal, showed that chemical interaction is restricted to the surface of the coal grains. In other studies[313] on coal carbonization, the distribution of S^{35}, added as labeled $Fe_2(SO_4)_3$, was measured.

Storage, Handling, Transportation, and Use

The use of radioisotopes for level measurement in large containers is now very widespread. Red China has reported the use of gamma gages for measuring and automatically controlling the minimum and maximum levels of coal in storage bins.[299] One device uses a Co^{60} source and operates with a count rate of 13 counts/sec at a distance of up to 2 m. Such a source must be replaced only every five years, thereby providing high reliability and minimum servicing. Similar devices are reported from, e.g., East Germany,[314] West Germany,[315] and the USSR.[292]

In East Germany, radioisotopes are used in controlling coal movement, e.g., for braking a train on passing a signal in the "stop" position, in rear signaling, and in automatic controlling of block signals.[316] Cobalt-60 sources are attached either to the train or to stationary signal masts, and the gamma detectors are placed on the other part. The radiation circuit is part of an electronic circuit, which in turn controls either the brakes or the signals. In West Germany, radioisotopic devices control the automatic loading and unloading of cars, which dump the coal without stopping.[315]

The West Germans have used Co^{60}, Cs^{137}, and Ir^{192}, strong gamma emitters, to determine crust formation in pipes.[315]

A method for automatic routing and keeping a more accurate record of the location of either whole coal trains or individual cars has been described.[317] The cars are marked underneath with various combinations of radioisotopes, to uniquely identify them, and a radiation detector is mounted under the track and connected to operate automatic switching facilities. Such a system would operate reliably under all environmental conditions, even at low temperatures

and under ice and snow. The results of a 1959 Japanese test of such a signal system[318] indicated that it was simpler, lower in cost, better able to distinguish train type and speed, and more reliable in operation under adverse conditions, e.g., snow and gravel, than the conventional contact system. In this test a 1-mc Co^{60} (5.3-year) gamma source was sealed in a pig-iron container and installed under a train car. A G-M counter in a brass case was buried underground between the two rails. When the car with the source passed over the detector, the detector pickup triggered a relay circuit, which sent out control signals. For the system used, 20 cm between the source and detector was the optimum distance. The system worked properly up to train speeds of 55 km/hr.

The Polish Mining Institute designed a hydraulic pipeline for transporting coal slurries 100 miles.[319] If this pipeline should be economically competitive, strong gamma emitters may be introduced into the slurry, or by-flow samples may be irradiated with neutrons, and the induced radioactivity determined as a function of distance for control of flow rate and measurement of density. However, a recent visitor to Poland reported that this pipeline is still under construction and will carry only 5-mm coal particles for 72 km.

The Japanese have devised a radioisotopic method for automatic control of combustion in a steam power generator.[320] The instantaneous concentration of the pulverized coal in pneumatic conveyors is measured by the soft-beta radiations of Kr^{85} (10.6 years) and Tl^{208} (3.9 years). The concentration was varied from 0.2 to 1.3 kg per cubic meter of air, and flow conditions were measured at six points.

Testing and Analysis

The Japanese use[321] a Fe^{55} source and tritium bremsstrahlung to determine the ash content of coal samples by X-ray fluorescence. Agreement with values obtained by the classical electric-furnace combustion method is good. The results of a Russian[322a] method for determining ash based on attenuation of the bremsstrahlung from the pure-beta emitter Tl^{204} (3.9 years) indicate that moisture content, chemical composition of the ash, especially the high heavy-metal content, and degree of beam collimation have a strong effect on the values obtained.

A Russian[322] beta backscatter method in which a 50-mc Sr^{90} (28-year) pure-beta source was used for ash determination showed an average error of 0.1% under industrial field conditions when tested with standard samples prepared from coal containing 7.8% ash and a mineral with 74.4%. Individual measurements were completed in 1 min. Results of a beta backscatter method are reported[322b] to be the same as those obtained with a gamma-absorption method carried out with a Tm^{170} source. Beta backscatter ash determinations made[323] in Japan on 28 brands of coal with 6 to 30% ash were so much faster than gravimetric measurements that the Japanese built an apparatus for continuous determination of coal ash. An East German study on the effect of sand, clay, and pyrites variations on the accuracy of the beta backscatter method showed that the effect was most marked for pyrites: Addition of 1% pyrites produced the same effect on the reading as 3% sand or clay.[324] In this work the changes in the backscatter intensity from a 50-μc $Sr^{90} + Y^{90}$ beta source were determined as a function of ash content. An aluminum-metal-foil filter markedly increased the sensitivity of the method. The average time required for one analysis was 10 min, and the mean error, 1%.

A working model for a gamma-ray attenuation method for ash-content determination was developed[325] in Czechoslovakia, and a working model was demonstrated at the Moscow Fair in 1959. It was most efficient with Tl^{204}, Tm^{170} (127-day, beta-gamma), Th^{232} (1.4×10^{10}-year, alpha-gamma), and Se^{75} (120-day, pure-gamma) sources. In Hungary[326] gamma absorption has been used to measure the ash content of coal in the Pecs region, with the advantages of continuous measurement, rapid accessibility of data, and increased accuracy. In Japan,[327] Co^{60} (5.3 years, gamma), Cs^{137} (30 years, gamma), Ce^{144} (284 days, beta-gamma), and Tm^{170} have been used for ash-content measurements.

Radioisotopes may also be used in determining the caloric value of coal. Of the Soviet Bloc countries, only the Hungarians seem to have published their work.[326,328] Since the relation between density and calorific value of coal is close, it was natural that gamma radiation should be used for determining the heat obtainable from coal, and Tm^{170} has been used for this purpose. This weak gamma emitter was chosen because only small density differences were expected. Measurement depends on com-

pression variables, e.g., grain size and pressure. Results were best with air-dried material.

The Japanese have developed an X-ray absorption method for measuring calorific value.[321] A tritium-titanium source-target is used, and a working curve is obtained for each separate brand of coal. Results obtained are comparable to those obtained by classical procedures.

Research

The Russians have reported[329] a method of measuring gear-wheel wear in which the pinions are labeled with Zn^{65} (235-day, beta-gamma) tracer. Tracers generally were found to be very efficient in lubricant evaluation and gave reliable data in a short time.

Interesting investigations reported[330] from Japan in 1959 involve the use of radioisotopes in the transmission testing of heavy fluid materials, in the Baum jig applied test, and in the evaluation of particle size and density of coal. Density, coal thickness, and ash content strongly affect transmission of the particles.

In order to better understand the structure of coal and the nature of the coal carbonization process, significant investigations[331] have been carried out in the Netherlands with "artificial coal" tagged with C^{14}. In one series of investigations, condensed polycyclic aromatic hydrocarbons containing C^{14} atoms were synthesized and studied radiographically after being carbonized under various conditions of heat and pressure. In another study C^{14}-labeled formaldehyde was introduced into the highly condensed macromolecule, and the number of $HC^{14}HO$ units contained in the condensed structures was determined. These studies confirmed the prevailing concepts about the structure of coal and the processes taking place during carbonization.

Instrument Development

The expanded use of tracers in lower concentrations as well as for new applications depends upon the availability of more sensitive and versatile radiation detectors. In an effort to promote this area of development, the Division of Isotopes Development sponsors several programs in instrument research. Two of these are described in this section: (1) the use of a Geiger counter to determine tritium as water vapor and (2) the use of scintillating fibers in counting.

Geiger Counting of Tritium as Water Vapor

Most tritium samples are in the form of water. Ely and Ballard,[332] in a study done recently at Research Triangle Institute under a Division of Isotopes Development contract, demonstrated that water vapor plus Q-gas (98.7% helium, 1.3% butane) could be used as a Geiger mixture in a heated system. For water-vapor pressures up to 300 mm Hg, the efficiency of this counting technique is 80 to 90%, depending on the counter.

A flow-counting method developed by these workers is applicable to continuous tritium-tracer monitoring for either process control or health physics. The sensitivity of the method is greater than present ion-chamber techniques, which also suffer from the inability to distinguish between tritium and other radioactive gases. Table II-13 is a comparison of the sensitivity of various counting methods, including the Geiger vapor-counter method described here.

In earlier work, small amounts of water vapor were counted by mixing with other gases.[334,335] Butler[336] determined counting characteristics of Q-gas saturated with water vapor at 22.5°C (20 mm Hg) and obtained slopes of 3.4% per 100 volts and plateaus 400 volts long. Cameron[337] obtained a counting efficiency of 98% for water vapor at room temperature in an argon-alcohol mixture, whereas Joshi[338] found that the 300-volt plateaus of argon-hydrogen and argon-ether counters disappeared at 52°C. In the Ely and Ballard work, plateaus were several hundred volts long, and for low counting rates the slopes ranged from 0.03 to 0.08% per volt.

Materials and Methods. Six counters were used in various phases of this study: two of glass, three of copper, and one of stainless steel. The glass counters were unsatisfactory, and operation of the copper counters became erratic after several months of use. The steel counter was used longer than any other without showing signs of deterioration. As shown in the construction drawing of the steel counter, it had an effective volume of 380 ml (Fig. II-20). Both batch and flow systems were investigated with these counters. An unmodified Nuclear-Chicago

Table II-13 SENSITIVITY OF TRITIUM COUNTING METHODS FOR WATER

(Conditions: σ = ±10%, Sample Counting Time = Background Counting Time = 30 Min)

Method	Counter vol., ml	Pressure	Efficiency, %	Background	Sample wt., g	Sensitivity, dis/(min)(g of H_2O)
Liquid scintillation[333]	10		7	50 counts/min	0.37	770
	50		7	75	1.8	190
Ion chamber[333]	500	1 atm H_2	80	3×10^{-17} amp	0.37	480
Geiger vapor counter (unshielded)	500	450 mm Hg	68	280 counts/min	0.17	390†
Geiger vapor counter (shielded)	500	450 mm Hg	68	80 counts/min	0.17	220†
Geiger vapor counter (anticoincidence)	500	450 mm Hg	68	8 counts/min*	0.17	80†
Low-level gas counter (anticoincidence)	500	2 atm H_2	100	8 counts/min*	0.74	16†

*A nominal background; individual counters vary from 2 to 20 counts/min.
†Calculated from assumed background.

model 186 scaler with 250 mv sensitivity was used for counting.

Figure II-21 is a sketch of the apparatus used in the batch method with a 2- by 12-in. copper counter. In this system the water sample vial, attached by a tapered joint, was heated to the desired temperature; the counter was degassed by allowing two expansions of water vapor into it, and then evacuated and closed off from the vacuum system. First Q-gas, then the water-vapor sample, was allowed to expand into the counter to the desired total pressure.

Figure II-22 shows the design of the equipment for the flow-counting method. No vacuum pump was needed in this system. A 2-ml water sample was inserted in a fritted disk funnel by hypodermic needle, and Q-gas was introduced through the bottom of the frit. Condensation in the counter and associated system was prevented by maintaining all portions at a temperature above that of the sample. Flow was controlled with a low-pressure regulator and a metering valve. The sample vial was submerged in the water bath at a temperature corresponding to the desired vapor pressure. Variation in the bath temperature was ±0.25°C. The Q-gas was warmed before entering the funnel by passing it through about 5 ft of $^3/_{16}$-in.-diameter copper tubing immersed in the water bath. All parts of the system between the sample vial at the inlet and the ice bath at the exit were held at about 100°C. The ice bath at the exit was used to collect the sample for rerun or disposal.

In the flow-counting system, the sample, before being counted, was purged of dissolved gases by flowing Q-gas through it at a rate of 75 cm^3/min, and 10 min was allowed for the sample temperature to come to equilibrium before counting was started.

In both the batch and flow systems, the partial pressure of the water vapor was controlled by the temperature of the water sample.

The efficiency was determined by comparison with a National Bureau of Standards sample, from which two standards were made with activities differing by a factor of 10. Dilution

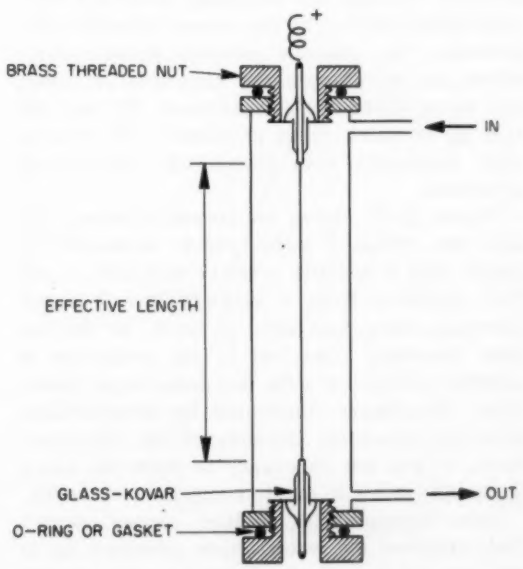

Fig. II-20 Construction of stainless-steel counting tube.

and decay corrections gave activities of 184,000 and 18,400 dis/(min)(ml) for the standards used with a copper counter. The less-active sample had decayed to 18,200 dis/(min)(ml) when used in the stainless-steel counter.

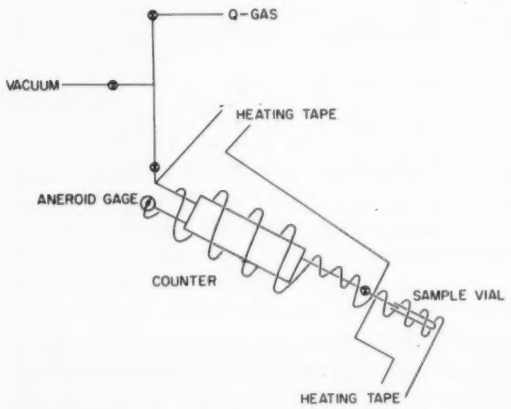

Fig. II-21 Schematic representation of system for batch counting of tritium as water vapor.

Results. Batch System. With the batch method the slope and length of the counting plateau were largely a function of the amount of Q-gas present in the counter. On the other hand, the starting voltage and counting efficiency were determined largely by the amount of water vapor present. The plateaus became progressively worse as the water-vapor pressure increased and disappeared entirely between 400 and 500 mm Hg of water-vapor pressure. The counting rate increased with increasing water-vapor pressure.

Figure II-23 shows the plateau counting rate and the tritiated water-vapor pressure for water with a specific activity of 0.075 μc/ml. The deviation from a straight line at higher counting rates was due, in part, to the 200 μsec recovery time and to the reduction in counting efficiency with increased vapor pressure. This figure illustrates the independence of Q-gas pressure. Because of this independence, it was not necessary to know the exact Q-gas pressure to obtain reproducible results.

Data obtained with another copper counter that extended the water-vapor pressure up to 450 mm Hg and the total gas pressure to 750 mm Hg showed that the plateau counting rate approached a maximum value; additional water vapor was completely offset by the decrease in efficiency of the counter.

A plateau of sorts did exist for water vapor alone for pressures up to about 300 mm Hg; by comparison, however, a plateau with 500 mm of Q-gas added to 300 mm Hg of water vapor was excellent. Variations in Q-gas pressure caused minor changes in the shape of the plateau.

At any given water-vapor pressure, the counting rate was a linear function of the tritium concentration of the water.

The cross-contamination between subsequent samples (memory) was negligible with the copper counter used in the batch work.

Flow System. As with the batch system, the most striking result of the addition of the water vapor to Q-gas was its effect on the threshold voltage. This effect (Fig. II-24) indicated that saturation was occurring and that the bath temperature was a true measure of vapor pressure.

Plateaus were several hundred volts in length with the larger counters (Fig. II-25). Overvoltage normally was not more than 150 to 200 volts, but this value was exceeded in the steel counter without apparent ill effect. For low counting rates the slopes were from 0.03 to 0.08% per volt, but for high counting rates there was a characteristic hump, which flattened slightly at increased total pressure and was apparently associated with recovery time.

Background remained normal in the steel counter at all vapor pressures, even when it

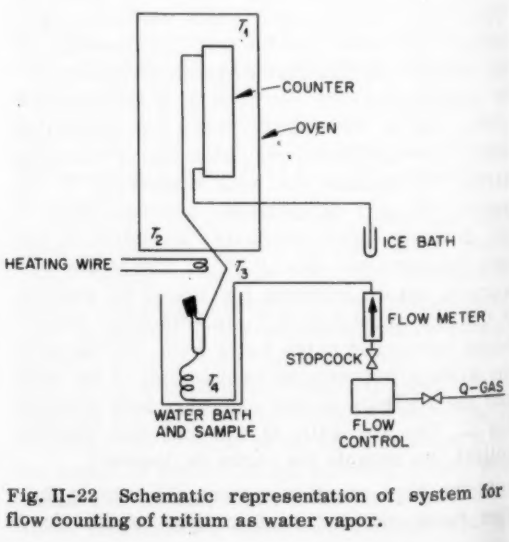

Fig. II-22 Schematic representation of system for flow counting of tritium as water vapor.

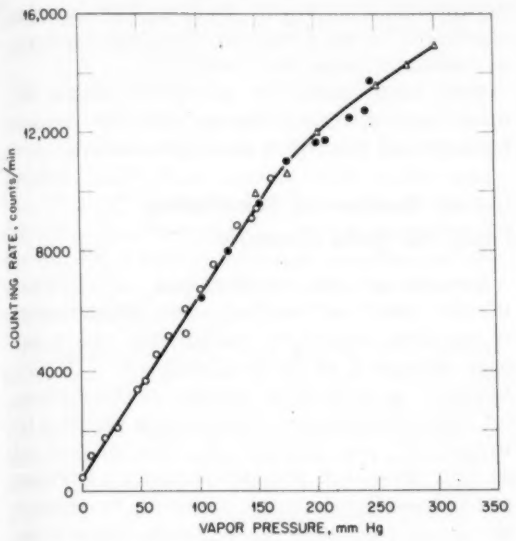

Fig. II-23 Counting rate of tritium as a function of Q-gas and vapor pressure with the batch system. The Q-gas pressure was: ○, 600 mm; ●, 500 mm; △, 450 mm.

was operating near 5000 volts. By contrast, once a discharge had occurred in the copper counter, the background plateau was poor at pressures above 200 mm Hg.

Efficiency was about 90% at water-vapor pressures up to 200 mm Hg in the copper counter and about 80% up to 380 mm in the steel counter. It then decreased gradually with increasing vapor pressure down to about 60%, where the plateau deteriorated. Figure II-26 shows the tritium counting rates for two different specific activities and increasing vapor pressures.

The recovery time of the counter was a function of vapor pressure, overvoltage, and counter temperature, the recovery time being less at higher temperature. The maximum recovery time of 400 to 450 μsec occurred at higher overvoltages for increased water-vapor pressure. Coincidence corrections were less than 1% for counting rates below 1200 counts/min.

Sensitivity. The sensitivity of the flow counter was defined as the minimum specific activity of water that would give a net counting rate having a standard deviation of 10% for a sample and background counting time of 30 min each. The data are shown in Fig. II-27. The counters in this study were unshielded and gave maximum sensitivities for tritium counting of about 450 dis/(min)(ml) of water for a background counting rate of about 250 counts/min. Thus the vapor counter is somewhat more sensitive than either the shielded ionization chamber or the 10-ml liquid scintillation counter (Table II-13), and with shielding it should compare favorably with the large liquid scintillation counter. The sensitivity obtained by anticoincidence operation of the vapor counter, because of problems associated with heating the counter in a necessarily large shield, places it at a disadvantage with respect to the low-level gas counter even though conversion to hydrogen is not required. With a total pressure of 750 mm Hg, satisfactory Geiger plateaus were obtained for water-vapor partial pressures of 350 to 450 mm Hg, depending on the counter used.

Pulse height in the plateau region increased with increased vapor pressure. When Q-gas alone was used, the pulse height was about 5

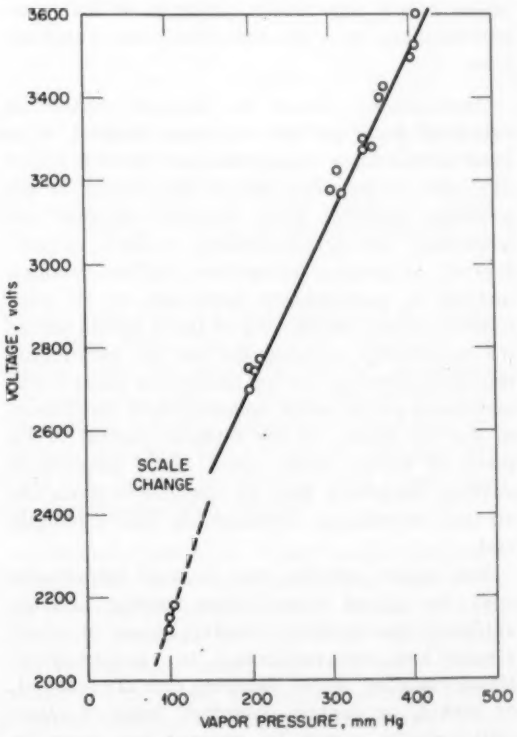

Fig. II-24 Effect of vapor pressure on threshold voltage in the flow system. A 1¾-in.-diameter copper counter with a 3-mil tungsten anode was used.

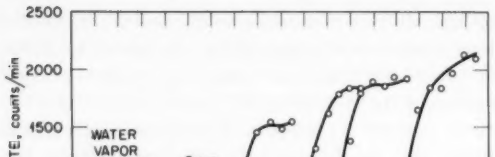

Fig. II-25 Plateaus at various water-vapor pressures and voltages. Total pressure, 1 atm. The stainless-steel counter had a 3-mil molybdenum anode. Specific activity (A_s) was 1.82×10^4 dis/(min)(ml).

volts; with 100 mm Hg of water-vapor pressure, it was 10 volts; and at 400 mm all pulse heights were not equal in size until a voltage of 250 volts above threshold was reached, when they were 17 volts. The development of a single pulse height apparently occurred at the same overvoltage as does the maximum recovery time.

Applications. Since no vacuum system is required for the flow-counting method, it is most useful when enough sample (about 2 ml) is available to properly purge the system of the previous sample. When smaller samples are available, the batch-counting method is preferred. As pointed out earlier, the flow-counting method is particularly applicable to (1) continuous tracer monitoring at those levels where its sensitivity is adequate and (2) monitoring tritium content of air for biological hazard. The maximum permissible concentration for tritium in air is based on the tritium content in the form of water vapor. Thus, in a monitoring system, moisture may be condensed from the air and introduced continuously into a sample vial.

The vapor counter has certain advantages over the 10-ml scintillation counter and the shielded ion-chamber counter, some of which already have been mentioned. In present scintillation counting, water samples that are colored, or turbid, or contain dissolved salts or other radioactivity cannot be counted but must be purified by distillation before they can be introduced into the counter. In the vapor counter the process of introducing the sample performs this distillation. The vapor counter has simpler electronic circuits than the other two counters, in addition to being more sensitive.

The vapor technique should be useful for urine analysis for tritium, with the sample being placed directly in the vial or funnel.

Use of Bundles of Scintillating Fibers for Beta Counting

Low-energy beta emitters (e.g., C^{14}, S^{35}, and H^3) are widely and routinely used. Measurement of this low activity by scintillating fibers has been suggested by several workers.[339–341] Recently, a system using bundles of these fibers for liquid scintillation counting was reported by Preston,[342] who worked on this project at Armour Research Foundation under a Division of Isotopes Development contract. The system has several advantages, including relative insensitivity to sample form and chemistry and the minimum time required for sample preparation. It also may be used as a flow counter that will retain much of the efficiency and energy proportionality of a liquid scintillation counter.

Preston, in his study of the influence of such parameters as fiber diameter, sample color, and index of refraction on efficiency, found that commercially available 0.5-mm-diameter fibers have an efficiency of 30% for C^{14} counting and that heavily colored solutions could be counted with 18 to 21% efficiency. He noted that sample volumes of 50 ml and some high-energy

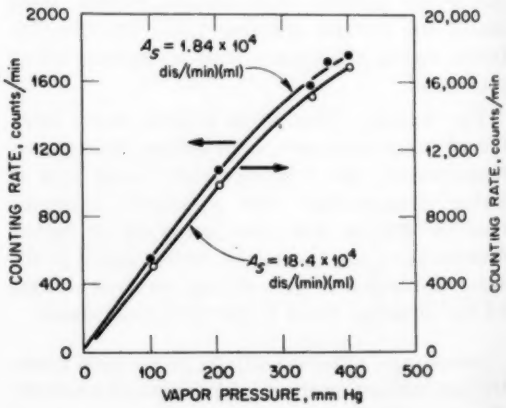

Fig. II-26 Effect of vapor pressure on tritium counting rate. The same counter as that in Fig. II-24 was used.

beta work probably could be achieved with an improved system.

Testing the Counter. The interstitial spaces between hexagonally close-packed fibers contain about 15% of the total volume of the bundle. Preston filled these spaces with a water solution of a C^{14}-containing compound and counted the activity. The counting system consisted of the bundle, a water-cooled photomultiplier tube at one end, amplifiers, and a multichannel pulse amplifier.

Commercially available plastic scintillating fibers with diameters of 0.1, 1.0, and 1.5 mm were tested. Bundles 1, 1.5, or 2 in. long by 0.5 in. wide were made from each diameter of fiber and were polished at each end with emery cloth and then with fine abrasive compound. They were placed in glass cylinders (0.5 in. in inside diameter by 2 in. in length) equipped with inlets and outlets for filling. End windows of glass having a refractive index of 1.5188 were used to seal off the cylinders, and the ends of the bundles were sealed to the windows with a thin coating of coupling compound.

Sample volume was obtained with the fiber array in place by filling the housings with water from a hypodermic syringe. The volume of the water was rechecked after removal. Once the volume of each unit was determined, it was filled with a calibrated, standard liquid C^{14} source. The unit was then coupled to the photomultiplier tube. The counting efficiency was studied with ink added to the C^{14} solution to determine the value of the technique with nontransparent sample solutions. Both clear and colored samples were removed satisfactorily from the system by passing cold water, then air, through the fiber bundle.

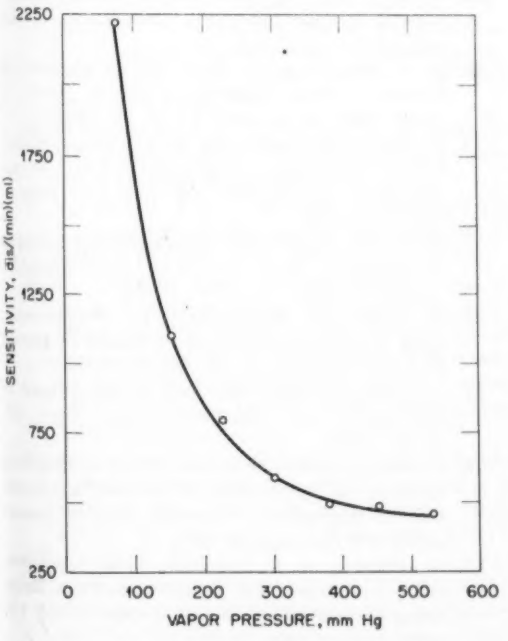

Fig. II-27 Effect of water-vapor pressure on sensitivity. Sens = S/mE, where S is the net sample counting rate that will give a standard deviation of 10% for a sample and background counting time of 30 min each, m is the grams of water in the counter, and E is the efficiency of the counter. An unshielded 380-ml 3-mil molybdenum-anode stainless-steel counter was used.

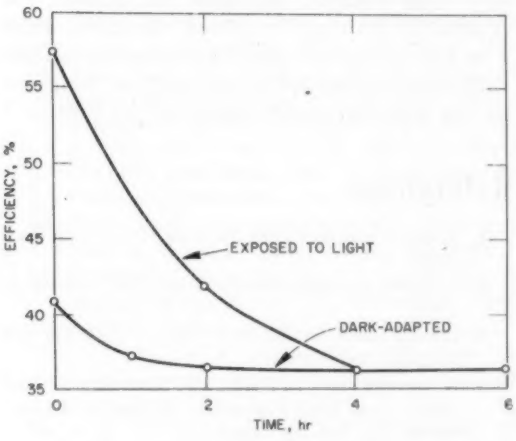

Fig. II-28 Efficiency as a function of stabilization time of fiber array exposed to room light and dark-adapted. Near-optimum size for fiber array and photomultiplier-tube high voltage were used. Fibers were 0.5 mm by 1.5 in.; high voltage, 1360 volts.

Optimum Conditions. Two major problems encountered were photomultiplier-tube noise and stabilization of the system. Tubes had to be carefully selected for optimum voltage gain with lowest dark noise, and they were water-cooled to increase the signal-to-noise ratio. Stability was achieved by dark adaptation of the counting system; sample changes were made in the dark and with the photomultiplier-tube voltage off, and 1 hr was allowed for stabilization.

The fiber which was 0.5 mm by 1.5 in. showed the greatest counting efficiency, with efficiency being defined as:

$$\frac{\text{(Integral counting rate of sample)} - \text{(background of system)}}{\text{(Actual counts in calibrated standard source of } C^{14} \text{ liquid)}}$$

Increasing the high voltage to the photomultiplier tube increased the efficiency.

The data in Fig. II-28 represent the near-optimum-size fiber array and photomultiplier-tube high voltage, and show the greatest reproducible efficiency achieved. As shown, about 4 hr was needed for stabilization before reliable data could be obtained in the light, as compared to 1 hr when the array was kept in the dark.

References

1. *Isotopes and Radiation Technol.*, 1(1): 53-64 (Fall 1963).
2. *Isotopes and Radiation Technol.*, 1(1): 64-74 (Fall 1963).
3. *Isotopes and Radiation Technol.*, 1(2): 160-174 (Winter 1963–1964).
4. G. Hevesy and F. Paneth, The Solubility of Lead Sulfide and Lead Chromate, *Z. Anorg. Allgem. Chem.*, 82: 323-328 (1913).
5. G. Hevesy, *Adventures in Radioisotope Research*, Pergamon Press, New York, 1962 (two volumes).
6. G. Hevesy, The Absorption and Translocation of Lead by Plants, *Biochem. J.*, 17: 439-445 (1923).
7. I. A. Christiansen, G. Hevesy, and S. Lomholt, Radiochemical Method of Studying the Circulation of Bismuth in the Body, *Compt. Rend.*, 178: 1324-1326 (1924).
8. G. Hevesy and E. Hofer, Elimination of Water from the Human Body, *Nature*, 134: 879 (1934).
9. G. Hevesy and E. Hofer, Diplogen (Deuterium) and Fish, *Nature*, 133: 495-496 (1934).
10. O. Chiewitz and G. Hevesy, Radioactive Indicators in the Study of Phosphorus Metabolism in Rats, *Nature*, 136: 754-755 (1935).
11. O. Chievitz and G. Hevesy, Studies on the Metabolism of Phosphorus in Animals, *Kgl. Danske Videnskab. Selskab, Biol. Medd.*, 13(9): 24 pages (1937).
12. G. Hevesy, J. J. Holst, and A. Krogh, Investigations on the Exchange of Phosphorus in Teeth Using Radioactive Phosphorus as Indicator, *Kgl. Danske Videnskab. Selskab, Biol. Medd.*, 13(13): 34 pages (1937).
13. S. W. Ferris, Determining the Wear of Surfaces Such as Bearings, Pistons, or Cylinders, U. S. Patent 2,315,845, Apr. 6, 1943 (Assigned to The Atlantic Refining Company).
14. G. L. Clark, S. G. Gallo, and B. H. Lincoln, Radiosulfur Tracer Study of Sulfurized Lubrication Addition Agents, *J. Appl. Phys.*, 14: 428-434 (1943).
15. B. W. Sakmann, J. T. Burwell, Jr., and J. W. Irvine, Jr., Measurements of the Adhesion Component in Friction by Means of Radioactive Indicators, *J. Appl. Phys.*, 15: 459-473 (1944).
16. J. E. Brugger, F. F. Rieke, and R. A. Semmler, Applications of Radioisotopes to Measurements of Piston Ring Wear and Evaluation of Engine Oils, USAEC Report TID-16050, Laboratories for Applied Sciences, University of Chicago, March 1962.
17. J. B. Warren, Jr., Means of Detecting Wear on Bits, U. S. Patent 2,468,905, May 3, 1949.
18. M. E. Merchant and E. J. Krabacher, Radioactive Tracers for Rapid Measurement of Cutting Tool Life, *J. Appl. Phys.*, 22: 1507-1508 (1951).
19. J. C. E. Button, A. J. Davies, and R. Tourret, A Study of Tracer Methods for Assessing Wear of Wire-Drawing Dies, *Nucleonics*, 9(5): 34-43 (1951).
20. V. P. Guinn, Following Large Scale Processes, *Nucleonics*, 14(5): 68-69 (1956).
21. D. E. Hull, The Total Count Technique: A New Principle in Flow Measurement, *Intern. J. Appl. Radiation Isotopes*, 4: 1-15 (1958).
22. D. E. Hull, J. W. Kent, and R. D. Lee, Radioactivity in Pipe Line Flow Studies, *World Oil*, 129(1): 187-188 (1949).
23. D. E. Hull, Dispersion and Persistence of Tracers in River Flow Measurement, *Intern. J. Appl. Radiation Isotopes*, 13: 63-73 (1962).
24. J. Kohl, R. D. Zenter, and H. R. Lukens, *Radioisotope Applications Engineering*, Chap. 10, pp. 324-340, D. Van Nostrand Company, Inc., Princeton, N. J., 1961.
25. D. E. Hull, Radiotracer Studies of Flow Patterns in Industrial Plants, *Intern. J. Appl. Radiation Isotopes*, 1: 305-313 (1957).
26. A. Gemant, E. Hines, and E. L. Alexanderson, Leak Location by Radioactive Gases in Buried Pipes, *J. Appl. Phys.*, 22: 460-464 (1951).
27. A. Gemant, Tracer Diffusion in the Ground in Radioactive Leak Location, *J. Appl. Phys.*, 24: 93-95 (1953).
28. L. W. Hill, Development of a Method of Detecting Leaks in the Sheathing of Telephone Cable by the Use of Radioactive Materials, British Report AERE I/R 759, July 20, 1951.
29. S. Jefferson, J. F. Cameron, A. M. Wildblood, and J. L. Putman, Leak Detection in Water Mains Using Radioisotopes, British Report AERE I/R 1693, January 1956.
30. A. Beerbower, E. O. Forster, J. J. Kolfenbach, and H. G. Vesterdal, Evaluation of Mixing Efficiency of Processing Equipment, *Ind. Eng. Chem.*, 49: 1075-1078 (1957).
31. B. A. Fries, D. E. Hull, and S. B. Jones, Radioisotopes Solve Five Refining Problems, *Oil Gas J.*, 54(75): 268-269, 271 (1956).

32. R. E. McMahon, Radiotracer Study of Coke Formation on Cracking Catalyst, *Ind. Eng. Chem.*, 47: 844-845 (1947).
33. R. A. Fookes, J. S. Watt, and J. A. Warburton, A Radioisotope Technique for Tracing air Movements in Clear Air and in Clouds, *Nature*, 196: 328-329 (1962).
34. M. I. Kalkstein, Rhodium-102 High Altitude Tracer Experiments, *Science*, 137: 645-652 (1962), and M. I. Kalkstein, Rhodium-102 High Altitude Tracer Experiment I. Stratospheric Results, Report AFCRL-62-460(I), Air Force Cambridge Research Laboratories, July 1962.
35. L. Machta, Worldwide Radioactive Fallout from Nuclear Tests—Part II, *Nucl. Safety*, 5(1): 95-104 (especially pp. 103-104) (Fall 1963).
36. F. Begemann and W. F. Libby, Continental Water Balance, Ground Water Inventory and Storage Times, Surface Ocean Mixing Rates and World-Wide Water Circulation Patterns from Cosmic Ray and Man-Made Tritium, in *Radioisotopes in Scientific Research*, Vol. II, pp. 634-656, Proceedings of the First UNESCO International Conference, Paris, 1957, Pergamon Press, New York, 1958.
37. J. L. Putman and S. Jefferson, Applications of Radioisotopes to Leakage and Hydraulic Problems, in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955*, Vol. 15, pp. 145-150, United Nations, New York, 1956.
38. K. O. Beatty, J. K. Ferrell, and F. M. Richardson, Radioisotopes in the Study of Fluid Dynamics, *ibid.*, Vol. 15, pp. 194-198.
39. S. Inose, M. Kato, S. Sato, and N. Shiraishi, The Field Experiment of Littoral Drift Using Radioactive Glass Sand, *ibid.*, Vol. 15, pp. 211-219.
40. D. L. Inman and T. K. Chamberlain, Experiments with Radioactive Sand as a Tracer of Beach Sand Movement, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 19, pp. 349-354, United Nations, New York, 1958.
41. B. A. Fries, D. E. Hull, and R. J. Dupzyk, Radioisotopic Compounds Measure Fractionation in the Refinery, in *Proceedings of the Fifth World Petroleum Congress, New York, 1959*, Vol. 10, pp. 37-45, 1960.
42. J. M. Lambert, J. H. Roecker, J. J. Pescatore, G. Segura, Jr., and S. Stigman, How to Prepare and Use Radioactive Soils, *Nucleonics*, 12(2): 40-42 (1954).
43. F. Ehrenkranz and E. H. Jebe, Carbon-14 Method Tests Home Laundering Procedures, *Nucleonics*, 14(3): 96-101 (1956).
44. D. B. Todd and W. B. Wilson, Stack Loss of Catalyst from Commercial Catalytic Cracking Units, *Ind. Eng. Chem.*, 49: 20-24 (1957).
45. W. B. Wilson, G. M. Good, T. J. Deahl, C. P. Brewer, and W. G. Appleby, Commercial Performance of Fluid Cracking Catalysts, *Ind. Eng. Chem.*, 48: 1982-1989 (1956).
46. J. Kohl, R. D. Zenter, and H. R. Lukens, *Radioisotope Applications Engineering*, Chap. 13, pp. 393-410, D. Van Nostrand Company, Inc., Princeton, N. J., 1961.
47. Radioisotopes in Hydrology: An IAEA Symposium, *Nucleonics*, 21(5): 94 (1963).
48. *Radioisotopes in Hydrology*, Report STI/PUB/71, Proceedings of the Symposium on the Application of Radioisotopes in Hydrology, Held in Tokyo, March 5–9, 1963, International Atomic Energy Agency, Vienna, August 1963.
49. J. F. Kunc, Jr., Isotopes in the Petroleum Industry (Part of a Panel-Discussion on Uses of Isotopes in Industry), *Atomic Energy in Industry*, Fourth Annual Conference on Atomic Energy in Industry, New York, 1955, National Industrial Conference Board, Inc., New York, 1956.
50. W. H. King, Jr., Radioisotopes in Petroleum Refining, *Ind. Eng. Chem.*, 50: 201-214 (1958).
51. E. Singer, D. B. Todd, and V. P. Guinn, Catalyst Mixing Patterns in Commercial Catalytic Cracking Units, *Ind. Eng. Chem.*, 49: 11-19 (1957).
52. D. E. Hull, B. A. Fries, J. G. Tewksbury, and G. H. Keirns, Isotopes Solve Mixing Problems, *Nucleonics*, 14(5): 50-51 (1956).
53. D. E. Hull, B. A. Fries, J. G. Tewksbury, and G. H. Keirns, Mixing in Surge Tanks and Stills, *Nucleonics*, 14(5): 51-53 (1956).
54. V. P. Guinn, Tracing Catalysts in Refinery Crackers, *Nucleonics*, 14(5): 69-72 (1956).
55. R. N. Bartholomew and R. M. Casagrande, Measuring Solids Concentration in Fluidized Systems by Gamma-Ray Absorption, *Ind. Eng. Chem.*, 49: 428-431 (1957).
56. A. J. Kinsella, Jr., and J. J. Mitchell, Better Catalyst-loss Studies, *Petrol. Process.*, 10: 1718-1723 (1955).
57. A. E. Handlos, R. W. Kunstman, and D. O. Schissler, Gas Mixing Characteristics of a Fluid Bed Regenerator, *Ind. Eng. Chem.*, 49: 25-30 (1957).
58. A. J. Brandel and D. E. Hull, Measure Vapor Losses with Radioisotopes, *Petrol. Refiner*, 37(3): 195-196 (1958).
59. D. E. Hull, Total Count Technique in the Refinery, *Ind. Eng. Chem.*, 50: 199-200 (1958).
60. G. F. Metcalf, Demarcation of Fluids in Pipelines, U. S. Patent 2,631,242, Mar. 10, 1953 (Assigned to General Electric Company).
61. D. E. Hull, Fluid Flow Measurement, U. S. Patents 2,826,699 and 2,826,700, Mar. 11, 1958 (Assigned to California Research Corp.).
62. J. J. Mitchell and A. J. Kinsella, Jr., Study of Catalyst Flow in Fluid Catalytic Cracking by Means of Radioactive Tracers, U. S. Patent 3,039,975, June 19, 1962 (Assigned to Texaco, Inc.).

Specific Tracer and Radiochemical Applications

63. Wm. H. Johnston, Basic and Applied Radiotracer Studies, USAEC Report JLI-2748-0-5, William H. Johnston Laboratories, Inc., June 1, 1962.
64. Wm. H. Johnston, H. P. Yule, and J. H. Carpenter, An Ultrasensitive Analyzer for Measuring Speed of Water Current, *Trans. Am. Nucl. Soc.*, 5: 276-277 (1962).
65. Wm. H. Johnston, High Dilution On-Stream Isotopic Tracers, USAEC Report JLI-2748-0-7, William H. Johnston Laboratories, Inc., Mar. 29, 1963.
66. *Isotopes and Radiation Technol.*, 1(1): 24 (Fall 1963).
67. K. E. Wilzbach, Tritium-Labeling by Exposure of Organic Compounds to Tritium Gas, *J. Am. Chem. Soc.*, 79: 1013 (1957).
68. S. Rothchild (Ed.), *Advances in Tracer Methodology*, Vol. I, Plenum Press, New York, 1963.
69. *Tritium in the Physical and Biological Sciences*, Report STI/PUB/39, Proceedings of the Symposium on the Detection and Use of Tritium in the Physical and Biological Sciences, Held in Vienna, May 3–10, 1961, International Atomic Energy Agency, Vienna, 1962 (Vol. I, Physics and Chemistry; Vol. II, Biology).
70. P. M. Yavorsky and E. Gorin, Utilization of Radioactive Isotopes in Coal Process Research, USAEC Report NYO-9143, Consolidation Coal Company, Apr. 30, 1961.
71. P. M. Yavorsky and E. Gorin, New Reagent for Labeling Organic Compounds with Tritium, *J. Am. Chem. Soc.*, 84: 1071-1072 (1962).
72. E. E. Fowler and P. C. Aebersold, New Improved Tritiation Method for High-Molecular-Weight Organic Compounds, *Isotopes and Radiation Technol.*, 1(1): 25-26 (Fall 1963).
73. P. M. Yavorsky and E. Gorin, Development of Tritium Labeling of Organic Materials, USAEC Report NYO-10178, Consolidation Coal Company, June 20, 1963.
74. S. Olsson, Acid-Induced Aromatic Hydrogen Exchange. I. Determination of the Exchange Rates of Deuterium and Tritium Against Protium in Benzene and Toluene, *Arkiv Kemi*, 14: 85-98 (1959).
75. V. Gold and D. P. N. Satchell, The Kinetics of Hydrogen Isotope Exchange Reactions. II. The Reaction Between Para-Substituted [o-^{2}H] Phenols and Aqueous Sulphuric Acid, *J. Chem. Soc.*, 1955: 3609-3618.
76. G. J. Angele, Prevention and Control of Cross Connections at Oak Ridge, Tenn., Nuclear Plant, *J. Am. Water Works Assoc.*, 50: 628-638 (1958).
77. J. N. Baird, Jr., W. R. Sanford, and G. A. Cristy, Evaluation of a Reduced Pressure Backflow Preventer Using Activation Analysis, USAEC Report ORNL-3380, Oak Ridge National Laboratory, Dec. 26, 1962.
78. L. C. Bate, Y. Wellwart, and J. R. Stokely, A Rapid Chemical Separation for Radiomanganese, USAEC Report ORNL-TM-438, Oak Ridge National Laboratory, Dec. 6, 1962.

Use of Isotopes in the Food-Canning Industry

79. *a. The Canning Industry*, 5th ed., 1963, National Canners Association, Washington, D. C.
    b. Canners Directory, 1963–1964 ed., National Canners Association, Washington, D. C.
80. I. I. Somers, Canned Foods in the Civil Defense Program, *Activities Report, Armed Forces Food and Container Institute*, 14(2): 68 (1962).
81. Campbell Soup Company, Department of Agricultural Research, Riverton, N. J., *Annual Reports*, 1960.
82. J. K. Hammes and J. F. Bartz, Root Distribution and Development of Vegetable Crops as Measured by a Radioactive Phosphorus Injection Technique, *Agron. J.*, 55: 329 (1963).
83. *Chem. Eng. News*, 41(47): 102 (1963).
84. R. W. Hatch and G. M. Reid, Biological Laboratory, Auke Bay, Alaska, unpublished results, 1960–1963. (This work will be reported in detail in: W. A. Mercer, Radioisotopic Tracer Techniques in Evaluation and Improvement of Industry Practice in Removal of Pesticide Residues from Foods, Annual Report, USAEC Report SAN-1023, National Canners Association, February 1964.)
85. W. G. Jennings, A. A. McKillop, and J. R. Luick, Circulation Cleaning, *J. Dairy Sci.*, 40: 1471 (1957).
86. G. L. Hays, J. D. Burroughs, and D. H. Jones, The Cleanability of Materials in Contact with Dairy Products, *J. Milk Food Technol.*, 21: 68 (1958).
87. *a.* R. K. Sanders, in *Recent Advances in Food Science*, Vol. I, p. 146, J. Hawthorn and J. M. Leitch (Eds.), Butterworths, London, 1962.
    b. D. H. Berryhill, California Packing Corporation, private communication, Jan. 6, 1964.
    c. V. E. Banashek, Radioactive Method of Automatic Regulation of Densities in the Food Industry (in Russian), in *Transactions of Scientific-Technical Conference, Riga, 1959*; also in USAEC Translation AEC-tr-4139.
88. W. A. Mercer, Radioisotopic Tracer Techniques for Detection and Measurement of Detergent Residues on Washed Foods, Annual Report, USAEC Report SAN-1020, National Canners Association, April 1962.
89. W. A. Mercer, Radioisotopic Tracer Techniques in Evaluation and Improvement of Industry Practice in Removal of Pesticide Residues from Foods, Annual Report, USAEC Report SAN-1022, National Canners Association, February 1963.
90. *Isotopes and Radiation Technol.*, 1(2): 181-188 (Winter 1963–1964).

91. B. E. Proctor and S. A. Goldblith, Electromagnetic Radiation Fundamentals and Their Application in Food Technology, *Advan. Food Technol.*, 3: 120-189 (1951).
92. B. A. Morgan and J. M. Reed, Resistance of Bacterial Spores to Gamma Radiation, *Food Res.*, 19: 357-365 (1954).
93. C. B. Denny, C. W. Bohrer, W. E. Perkins, and C. T. Townsend, Destruction of *Clostridium botulinum* by Ionizing Radiation, Part I, *Food Res.*, 24: 44-50 (1959).
94. G. B. Pratt, E. W. Reaton, C. W. Bohrer, and C. B. Denny, Destruction of *Clostridium botulinum* by Ionizing Radiation, Part II, *Food Res.*, 24: 51-56 (1959).
95. E. Wheaton, G. B. Pratt, and J. M. Jackson, Radioresistance of Five Strains of *Clostridium botulinum* in Selected Food Products, *Food Res.*, 26: 345-350 (1961).
96. E. Wheaton and G. B. Pratt, Radiation Survival Curves of *Clostridium botulinum* Spores, *J. Food Sci.*, 27: 327 (1962).
97. R. A. Gillies, Organoleptic Evaluation of the Combined Effects of Heat and Radiation on Canned Peas, *Food Res.*, 27: 62-67 (1958).

Engine-Wear Studies with Radioisotopes

98. S. W. Ferris, Determining the Wear of Surfaces Such as Bearings, Pistons, or Cylinders, U. S. Patent 2,315,845, Apr. 6, 1943 (Assigned to The Atlantic Refining Company).
99. B. W. Sakmann, J. T. Burwell, Jr., and J. W. Irvine, Jr., Measurements of the Adhesion Component in Friction by Means of Radioactive Tracers, *J. Appl. Phys.*, 15: 459-473 (1944).
100. J. N. Gregory, Radioactive Tracers in the Study of Friction and Lubrication, *Nature*, 157: 443-444 (1946).
101. B. W. Sakmann, N. Grossman, and J. W. Irvine, Jr., A Study of Metal Transfer Between Sliding Surfaces, Report NACA-TN-1355, Massachusetts Institute of Technology, September 1947.
102. J. T. Burwell, Jr., Radioactive Tracers in Friction Studies, *Nucleonics*, 1(4): 38-50 (1947).
103. P. L. Pinotti, D. E. Hull, and E. J. McLaughlin, Application of Radioactive Tracers to Improvement of Fuels, Lubricants, and Engines, *S.A.E. Quart. Trans.*, 3: 634-638 (1949).
104. H. R. Jackson, F. C. Burk, L. J. Test, and A. T. Cowell, Some Phenomena of Engine Wear as Revealed by Radioactive Tracer Technique, *S.A.E. Quart. Trans.*, 6: 518-530 (1952).
105. H. R. Jackson, Laboratory and Field Tests Using Radioactive Tracers, *S.A.E. Trans.*, 61: 233-236 (1953).
106. J. T. Burwell and S. F. Murray, Radiochromium Plating for Friction Studies, *Nucleonics*, 6(1): 34-37 (January 1950).
107. M. Kerridge, Investigation of Wear of Metals by Radioactive Methods, in *Radioisotope Techniques, Proceedings of the Isotope Conference Oxford, England, July 1951*, Vol. 2, pp. 26-34, 1952.
108. J. C. E. Button, A. J. Davies, and R. Tourret, A Study of Tracer Methods for Assessing the Wear of Wire Drawing Dies, *ibid.*, pp. 34-46.
109. J. T. Burwell and C. O. Strang, Radioactive Tracers Reveal Friction and Wear of Metals, *Metal Progr.*, 60(3): 69-74 (September 1951).
110. E. Rabinowicz, A Study of Metal Transfer During Sliding, Using Radioactive Analysis, *Proc. Phys. Soc. (London)*, A64: 939-949 (1951).
111. E. Rabinowicz and D. Tabor, Metallic Transfer Between Sliding Metals: An Autoradiographic Study, *Proc. Roy Soc. (London)*, A208: 455-475 (1951).
112. F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solids*, Oxford University Press, London, 1954, and F. P. Bowden and D. Tabor, *Friction and Lubrication*, John Wiley & Sons, Inc., New York, 1956.
113. *Symposium on Radioactivity—An Introduction*, Special Technical Publication 159, American Society for Testing Materials, Philadelphia, 1954.
114. *Symposium on Radioisotopes*, Special Technical Publication 215, American Society for Testing Materials, Philadelphia, 1958.
115. *Symposium on Radioisotopes in Metals Analysis and Testing*, Special Technical Publication 261, American Society for Testing Materials, Philadelphia, 1960.
116. *Symposium on Applied Radiation and Radioisotope Test Methods*, Special Technical Publication 268, American Society for Testing Materials, Philadelphia, 1960.
117. V. N. Borsoff, D. L. Cook, and J. W. Otvos, Tracer Technique for Studying Gear Wear, *Nucleonics*, 10(10): 67-69 (1952).
118. F. W. Kavanagh, Engine Wear—Comparison of Radioactive Wear and Field Measurements, *S.A.E. Trans.*, 61: 231-232, 236 (1953).
119. A. Dyson and K. R. Williams, Symposium on Engine Testing of Lubricating Oils. The Use of Radioactive Tracer Technique in the Wear Testing of Engine Lubricating Oils, *J. Inst. Petrol.*, 39: 524-530 (1953).
120. M. Popovich and R. W. Peterson, *The Effect of Fuel Sulfur and Jacket Temperature on Piston Ring Wear as Determined by Radioactive Tracer*, Oregon State College, Engineering Experiment Station, Bulletin No. 33, Corvallis, 1953.
121. A. Hundere, G. C. Lawrason, and J. P. O'Meara, Neutrons, Gamma Rays, and Wear, *Lubrication Eng.*, 11: 230-237 (1955).
122. W. R. Miller and H. R. Jackson, Atoms Trace the Wear, *Lubrication Eng.*, 10: 238-241 (1955).
123. L. J. Gorry, Jr., Effect of Detergent and Dispersant Type Additives on Piston Ring Wear Using the Radioactive Technique, *Am. Chem. Soc., Div. Petrol. Chem.*, Preprint 1, No. 4: 20-25 (1956).

124. A. J. Snow and H. L. Skonecke, Radioactive Cutting Tool and Piston Ring Wear Tests, *Atompraxis*, 3: 299-306 (1957).

125. Yu. S. Zaslavskii, The Present Status of the Problem of Using Radioactive Isotopes and Radiations in the Petroleum Refining Industry, translated from *Khim. i Tekhnol. Topliv Masel*, 1: 5-15 (1959). Available as Report NP-tr-526 from the Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

126. B. Colding and L. G. Erwall, Accuracy and Applicability of Radioactive Studies of Carbide Cutting Tool Life, in *Proceedings of the Second Radioisotope Conference, Oxford, England, 1954*, Vol. 2, pp. 181-187, 1954.

127. B. A. Fries, D. E. Hull, and S. B. Jones, Applications of Radioactivity in Petroleum Technology, in *Proceedings of the Fourth World Petroleum Congress, Rome, 1955*, Sec. V, pp. 329-350.

128. Yu. S. Zaslavskii, Investigation of the Anti-Wear Properties of Oils and Fuels with the Aid of Radioactive Isotopes, in *Conference of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy, Moscow, 1955, Session of the Division of Technical Science*, USAEC Translation AEC-tr-2435, pp. 71-83.

129. E. P. Nadeinskaia, Use of Radioactive Isotope in Investigating Cutting Tool Wear, *ibid.*, pp. 85-95.

130. P. E. Diachenko and A. I. Nisnevich, Application of Radioactive Indicators for Evaluating the Wear of Piston Rings, *Vestn., Mashinostr.*, 35(7): 19 (1955). (This paper not yet obtained in translation.)

131. A. I. Nisnevich and S. A. Shchurov, Use of Radioactive Isotopes for Evaluating the Effect of Dust Present in Air on the Wear of Tractor Engines, *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk*, 7: 149-150 (1955). See also OID card 773 (this paper not yet obtained in translation).

132. A. I. Nisnevich, A Study of the Effect of Dust Upon the Deterioration of the Parts of a Tractor Motor, in *Proceedings of the All-Union Scientific and Technical Conference on the Application of Radioactive Isotopes, Moscow, 1957, Machine Building and Instrument Making*, USAEC Translation AEC-tr-4492, pp. 53-58.

133. D. Godfrey, Russian Research on Lubrication and Wear, *Lubrication Eng.*, 14: 27-31 (1958).

134. B. D. Grozin, The Use of Radioactive Isotopes in the Study of Wear of Machine Parts, in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955*, Vol. 15, pp. 160-166, United Nations, New York, 1956.

135. D. E. Hull and B. A. Fries, Radioisotopes in Petroleum Refining, Research, and Analysis, *ibid.*, Vol. 15, pp. 199-210 (especially pp. 207-208).

136. A. K. Hannum, Radioactive Tracers in Engine Research, *Thompson Prods. Eng. Bull.*, 1(2): 1-12 (1956).

137. R. G. Abowd, Jr., Chrome Face vs. Iron Side Wear — An Analysis of Some Radioactive Piston-Ring Wear Studies, *Am. Soc. Lub. Engrs. Trans.*, 1: 91-95 (1958).

138. M. E. Merchant, H. Ernst, and E. J. Krabacher, Industry Fights Wear with Isotopes, *Nucleonics*, 14(5): 54 (1956). Also, Tool-Wear Tests Speeded, *Nucleonics*, 14(5): 55-57 (1956).

139. V. I. Dikushin, The Application of Radioactive Isotopes in Machine Building, in *Proceedings of the All-Union Scientific and Technical Conference on the Application of Radioactive Isotopes, Moscow, 1957, Machine Building and Instrument Making*, USAEC Translation AEC-tr-4492, pp. 1-5. Also, see abstract on p. 73 of USAEC Translation AEC-tr-2925.

140. G. M. Zamoruyev and Ya. N. Levin, A Study of the Transfer of Metals During Friction and Deterioration, *ibid.*, pp. 28-34. Also, see abstract on p. 74 of USAEC Translation AEC-tr-2925.

141. G. V. Vinogradov, The Problem of the Transfer of Metals and of Materials Present on Their Surfaces, *ibid.*, pp. 35-36.

142. V. E. Vainshtein and Yu. M. Vinogradov, A Study of the Behavior of a Sulfided Layer in the Process of Deterioration, *ibid.*, pp. 20-27. Also, see abstract on p. 74 of USAEC Translation AEC-tr-2925.

143. M. M. Kusakov, G. V. Vinogradov, E. A. Razumovskaya, P. I. Sanin, and A. V. Ul'yanova, A Study of the Mechanism of the Reaction of Oil Additives with Metals, *ibid.*, pp. 76-81. Also, see abstract on p. 80 of USAEC Translation AEC-tr-2925.

144. Yu. S. Zaslavskii, S. E. Krein, R. N. Shneerova, and G. I. Shor, A Study of the Mechanism of the Action of Anticorrosive Additives to Oils, *ibid.*, pp. 69-75. Also, see abstract on p. 79 of USAEC Translation AEC-tr-2925.

145. M. Melik-Zade, An Apparatus for Studying the Formation of Films on Friction Surfaces, *ibid.*, pp. 96-98.

146. V. S. Zavelskii and K. S. Ramaiya, Study of the Effect of the Quality of Oil upon the Deterioration of Cast Iron, *ibid.*, pp. 40-47. Also, see abstract on p. 78 or USAEC Translation AEC-tr-2925.

147. V. I. Stetsenko and E. A. Markovskii, A Study of the Deterioration of High-Strength Cast Iron, *ibid.*, pp. 16-19. Also, see abstract on p. 74 of USAEC Translation AEC-tr-2925.

148. L. S. Palatnik, I. M. Lyubarskii, A. P. Lyubchenko, and V. G. Nesterenko, The Structure and Durability of Case-Hardened Steel, *ibid.*, pp. 6-15. Also, see abstract on p. 73 of USAEC Translation AEC-tr-2925.

149. V. P. Pavlov, G. V. Vinogradov, Yu. S. Zaslavskii, and F. B. Lebedev, A Study of Deterioration

During Rolling Friction, *ibid.*, pp. 37-39. Also, see abstract on p. 76 of USAEC Translation AEC-tr-2925.

150. M. D. Nikitin, The Relationship Between the Deterioration of a Diesel Engine's Upper Piston Ring and Cylinder Bush and the Engine Speed and the Maximum Pressure of the Cycle, *ibid.*, pp. 48-52. Also, see abstract on p. 76 of USAEC Translation AEC-tr-2925.
151. Yu. S. Zaslavskii, G. I. Shor, and I. A. Morozova, The Reduction of the Low-Temperature Deterioration of the Cylinder-Piston Group in Engines with the Use of Oil Additives, *ibid.*, pp. 59-68. Also, see abstract on pp. 78-79 of USAEC Translation AEC-tr-2925.
152. D. I. Vysotoskii, G. I. Beloglazov, V. I. Golov, V. P. Kaznacheev, and Yu. G. Mochalov, An Automobile Road Laboratory for Studying the Effect of the Dust Content of Air and the Quality of the Air Purifier on the Deterioration of the Engine's Piston Rings, *ibid.*, pp. 92-95.
153. R. Ya. Studnits, A Study of the Deterioration of Cogwheels in Coal-Mining Machines, *ibid.*, pp. 82-87. Also, see abstract on p. 81 of USAEC Translation AEC-tr-2925.
154. B. D. Lazebnik, Study of the Deterioration of Hard Alloy Cutting Tools, *ibid.*, pp. 112-116. Also, see abstract on p. 82 of USAEC Translation AEC-tr-2925.
155. G. M. Yakoviev, Study of the Deterioration of Cutting Tools, *ibid.*, pp. 117-122.
156. N. F. Kazakov, A Study of the Metal-Cutting Process, *ibid.*, pp. 104-111. Also, see abstract on p. 81 of USAEC Translation AEC-tr-2925.
157. A. I. Yudin, A Study of the Deterioration of Members of Feed Units in Airplane Engines, *ibid.*, pp. 88-91.
158. J. J. Gumbleton, F. L. Green, and W. J. Mayer, Transient Piston Ring Wear in Automotive Engines Using Fe^{59}, *Nucl. Sci. Eng.*, 7: 313-319 (1960).
159. F. L. Green and A. Somerville, Continuous Counting of Gamma Rays from Hot Radioactive Liquids, *Nucl. Sci. Eng.*, 7: 320-322 (1960).
160. J. P. Danforth and R. P. Stapp, *Radioisotopes in Industry Training Program* (two volumes), General Motors, Detroit, 1959. (Also available from the Office of Technical Services, U. S. Department of Commerce, Washington, D. C.)
161. C. C. Gambill, An Application of Radioisotope Wear Study Techniques, *Gen. Motors Eng. J.*, 5(2): 21-25 (April, May, June 1958).
162. F. T. Barwell, A Report of the Papers on Wear, in *Proceedings of the Conference on Lubrication and Wear, London, 1957*, pp. 587-601, Institution of Mechanical Engineers, London.
163. D. G. Christopherson, A Review of Hydrodynamic Lubrication with Particular Reference to the Conference Papers, *ibid.*, pp. 9-15.
164. C. B. Davies, A Review of Boundary Lubrication with Particular Reference to the Conference Papers, *ibid.*, pp. 319-325.
165. J. G. Withers, A Review of the Papers on I. C. Engine Lubrication, Miscellaneous Lubricants and Applications, and Additives, *ibid.*, pp. 493-497.
166. L. Grunberg and R. B. Campbell, Metal Transfer in Boundary Lubrication and the Effect of Sliding Velocity and Surface Roughness, *ibid.*, pp. 291-301.
167. J. K. Lancaster, Severe Metallic Wear, *ibid.*, pp. 694-700.
168. J. A. Edgar, Control of Wear in Piston Engines, *ibid.*, pp. 498-504.
169. M. E. Merchant, Cutting-Fluid Action and the Wear of Cutting Tools, *ibid.*, pp. 566-573.
170. R. B. Campbell, Sulfur as an Extreme Pressure Lubricant, *ibid.*, pp. 534-538.
171. A. Palmgren and B. Snare, Influence of Load and Motion on the Lubrication and Wear of Rolling Bearings, *ibid.*, pp. 454-458.
172. J. Golden and G. W. Rowe, A Radioisotope Study of the Effect of Surface Conditions During the Wear of Tungsten Carbide, in *Radioisotopes in Scientific Research*, Vol. I, pp. 343-361, Proceedings of the First UNESCO International Conference, Paris, September 1957, Pergamon Press, New York, 1958.
173. L. S. Palatnik, I. M. Ljubarsky, and A. P. Ljubchenko, On the Structure and Wear Resistance of Case-Hardened Steel, *ibid.*, pp. 375-387.
174. U. S. Landergren, A Radioactivity Method for Measuring Wear in Ball Bearings, *Intern. J. Appl. Radiation Isotopes*, 2: 86-88 (1957).
175. J. T. Burwell, Jr., Survey of Possible Wear Mechanisms, *Wear*, 1: 119-141 (1957).
176. R. B. Campbell and G. Harriden, Use of Radioactive Specimens on a Kinetic Boundary Friction Machine, *ibid.*, pp. 173-182.
177. M. W. Savage and L. O. Bowman, Radioactive Tracer Measurements of Engine Bearing Wear, *S.A.E. Trans.*, 65: 635-640 (1957).
178. D. G. Flom, Metal Transfer in Sliding Contacts, *J. Appl. Phys.*, 28: 850-854 (1957).
179. J. S. Batzold, J. V. Clarke, Jr., and J. F. Kunc, Radioactivity Traces Piston Ring Wear, *S.A.E. Trans.*, 66: 602-611 (1958). [Extracted in Continuous Radiotracer Monitoring Shows How Piston Rings Wear in Service, *S.A.E. J.*, 66(5): 81-83 (May 1958).]
180. P. J. Agius and R. E. Pegg, Using a Radioactive Liner for Studying Engine Wear, *Inst. Petrol. Rev.*, 12(142): 337-340 (October 1958).
181. A. Kohn, Use of Radioisotopes in Metallurgical Research and Industry, *Met. Rev.*, 3(10): 143-201 (1958).
182. R. A. Allen, The Uses of Radioactive Isotopes in Industry, *Steam Engineer*, 26: 383-386 (1957).
183. D. B. Smith, Radioactive Isotopes in the Study of the Wear of Machine Parts, *ibid.*, pp. 432-434.

184. R. L. Pontious, Determining Wear in Automotive Engines, *Lubrication Eng.*, 15: 110-115, 118 (1959).

185. R. Abowd, Jr., Radiotracer Technique Probes Adhesive Wear of Rings (an extract of Probing the Causes of Piston-Ring Wear by the Radiotracer Technique, presented at S.A.E. Annual Meeting, Detroit, January 12–16, 1959), *S.A.E. J.*, 67(3): 67-68 (1959).

186. E. E. Okrent and G. A. Weisgerber, A Radiotracer Counting Method for Engine Wear Determination, American Society of Mechanical Engineers, Lubrication Division, Annual Meeting, November 30–December 5, 1958, New York.

187. L. B. Shore and K. F. Ockert, Combustion-Chamber Deposits — A Radiotracer Study, *S.A.E. Trans.*, 66: 285-294 (1958).

188. D. E. Cooper, R. L. Courtney, and C. A. Hall, Radioactive Tracers Cast New Light on Fuel Distribution, *ibid.*, 67: 619-639 (1959).

189. V. P. Guinn and R. A. Coit, Measuring Oil Consumption with Tritium Tracers, *Nucleonics*, 17(12): 112-117 (1959).

190. B. A. Fries, F. J. Davis, and D. E. Hull, Radioactive Tracers for Engine Airflow Measurements, *S.A.E. J.*, 67(4): 87 (1959).

191. E. H. Loeser and S. B. Twiss, Analysis of Films Formed by Radioactive E-P Additives, *Lubrication Eng.*, 14: 343-349 (1958).

192. E. H. Loeser, R. C. Wiquist, and S. B. Twiss, Cam and Tappet Lubrication. III — Radioactive Study of Phosphorus in the EP Film, *Am. Soc. Lubr. Engrs. Trans.*, 1: 329-335 (1958).

193. E. H. Loeser, R. C. Wiquist, and S. B. Twiss, Cam and Tappet Lubrication. IV — Radioactive Study of Sulfur in the EP Film, *ibid.*, 2: 199-207 (1959).

194. M. J. Furey, Film Formation by an Antiwear Additive in an Automotive Engine, *ibid.*, 2: 91-100 (1959). See also *ibid.*, 2: 257-258 (1959).

195. T. Sata, Study of the Mechanism of Metal Wear by Use of Radioisotopes, in *Proceedings of the Second Conference on Radioisotopes, Japan, February 1958*, USAEC Translation AEC-tr-4482, pp. 220-235.

196. M. Kato et al., Research on Engine Wear by Use of Radioactive Tracers: Piston Rings Activated by Deuteron Bombardment, *ibid.*, pp. 236-251.

197. J. W. T. Spinks, Some Recent Applications of Isotopes in Research and Control in Industry, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 19, pp. 13-21, United Nations, New York, 1958.

198. A. V. Topchiev, I. T. Aladiev, and P. S. Savitsky, Applications of Radioisotopes, *ibid.*, Vol. 19, pp. 61-75.

199. A. V. Topchiev, A Survey of New Developments in Industrial Uses of Isotopes Reported to the Conference, *ibid.*, Vol. 19, pp. 101-106.

200. L. G. Erwall, Studies of Reactions at Solid-Liquid Interfaces and the Use of Radioactively Labelled Surface Layers, *ibid.*, Vol. 19, pp. 107-111.

201. W. W. Schultz, H. D. Briggs, R. A. Dewes, E. E. Godale, D. H. Morley, J. P. Neissel, R. S. Rochlin, and V. V. Verbinski, The Use of Activation in Making Isotope Techniques More Available to Industry, *ibid.*, Vol. 19, pp. 112-119.

202. J. H. Deterding and J. R. B. Calow, The Application of Radiotracers to the Measurement of Engine Wear in Moving Vehicles, *ibid.*, Vol. 19, pp. 141-146.

203. Yu. S. Zaslavskii, G. I. Shor, and R. N. Shneyerova, The Mechanism of Action of Anticorrosive Additives on Friction Studies, *ibid.*, Vol. 19, pp. 147-154.

204. D. Pavelesco (sic) and I. Iliuc, An Investigation by Radioactive Methods of the Effect of Viscosity on the Film Thickness of Lubricants, *ibid.*, Vol. 19, pp. 155-161.

205. M. J. Furey and J. F. Kunc, Radioisotopes in Fuel and Lubricant Research, in *Proceedings of the Fifth World Petroleum Congress, New York, 1959*, Vol. 10, pp. 59-74, 1960.

206. E. G. Stanford and J. H. Fearon (Eds.), *Progress in Non-Destructive Testing*, Vol. 2. See *The Uses of Radioactive Isotopes*, pp. 91-164, Heywood and Company, Ltd., London, 1960.

207. R. S. Rochlin and W. W. Schultz, *Radioisotopes for Industry*, Reinhold Publishing Corp., New York, 1959.

208. Battelle Memorial Institute, Systematic Abstracts of Current Literature, reprinted from *Battelle Technical Review* in *Wear*, 1: 254-271 (1957) and following issues.

209. *Program of the Third Japan Conference on Radioisotopes, Tokyo; 1959*, Cosponsored by: Japan Atomic Industrial Forum and Japan Radioisotope Association, Japan Atomic Industrial Forum, Inc., Tokyo, 1959.

210. M. Kato, S. Tsutano, Y. Takai, and A. Umehara, On the Study of Engine Wear Using Radioisotopes, Part 2: Availability of Piston Ring Activated by Neutron for Engine Wear Determination, Abstract T-11 59/P-11, Third Japan Conference on Radioisotopes, Tokyo, 1959.

211. T. Sakurai, M. Masuko, S. Ikeda, and H. Okabe, A Study of the Mechanism of Lubrication with the Extreme-Pressure Lubricating Oils Using S^{35} as a Tracer, Abstract T-9 59/P-9, *ibid.*

212. T. Sata and K. Nakajima, Study on Machinability of Materials by Radioactive Carbide Cutting Tools, Abstract T-10 59/P-10, *ibid.*

213. H. D. Briggs and J. F. Coultry, Measurement of Gear Wear by Activating Wear Particles in the Lubricant, *Chemical Engineering Progress Symposium Series, Vol. 56, No. 28, Nuclear En-*

gineering, Part VIII, pp. 76-79, American Institute of Chemical Engineers, New York, 1960.

214. W. P. Evans and E. W. Landen, Radioisotopes Can Do the Otherwise Impossible, Earthmoving, Engineers Say (an extract from Radioisotopes in Research, presented at S.A.E. Meeting, Central Illinois Section, April 15, 1959), *S.A.E. J.*, 67(8): 72-4D (1959).
215. M. K. Testerman, Use of Radioactive Iodine Vapor for Determining Surface Roughness, Report WADC-TR-59-659, University of Arkansas, December 1959. [Abstracted in *Wear*, 4: 89 (1961).]
216. J. Thiery, Improvements in the Use of Radiotracers for Studying Wear in Piston Segments (in French), *Intern. J. Appl. Radiation Isotopes*, 5: 197-203 (1959).
217. C. F. Jursch, P. L. Pinotti, and D. R. Jones, Radioactive Ring Wear Testing in Railroad Diesel Locomotives, in *Symposium on Applied Radiation and Radioisotope Test Methods*, Special Technical Publication 268, American Society for Testing and Materials, Philadelphia, pp. 3-14, 1960.
218. A. W. Crook, Some Studies of Wear and Lubrication, *Wear*, 2: 364-393 (1958–1959).
219. J. E. Howes, Jr., W. J. Braun, and D. N. Sunderman, The Use of Radiotracer Techniques to Study Lubrication and Wear in Large Diesel Engines, in *Proceedings of the Conference on the Use of Radioisotopes in the Physical Sciences and Industry, Copenhagen, 1960*, Report STI/PUB/20, Vol. 1, pp. 343-353, International Atomic Energy Agency, Vienna, 1962.
220. R. B. Campbell, L. Greenberg, A. A. Milne, and K. H. R. Wright, The Use of Radioactive Tracers in Lubrication and Wear Research, *ibid.*, pp. 355-368.
221. Yu. S. Zaslavskii and G. I. Shor, Radiotracer Method for the Study of the Working Properties of Lubricating Oils (in Russian), *ibid.*, pp. 369-380. See USAEC Translation AEC-tr-4410.
222. F. Frynta, F. Kkhol, and V. Kopetskii, Radioisotopic Control of Wear on the Suspension Bearings of Large Turbogenerators (in Russian), *ibid.*, pp. 381-385. See USAEC Translation AEC-tr-5189.
223. T. Sata, K. Abe, and K. Nakajima, Wear Studies in the Shearing Process by Means of Irradiated Tools, *ibid.*, pp. 387-396.
224. W. C. Arnold, V. T. Stonehocker, W. J. Braun, and D. N. Sunderman, Radioactive Cylinders—A Tool for Wear Research, *S.A.E. Trans.*, 68: 699-704 (1960).
225. J. J. Gumbleton, Four Considerations of the Radioactive Technique, *ibid.*, Suppl. 68: 5 (1960). (This is a discussion of the above paper of Arnold et al.)
226. J. Jaspert and A. Reuter, Measurements of Wear in Combustion Motors by Using Radioactive Isotopes and Spectroanalysis (in German), *Motortech. Z.*, 21(5): 181-183 (1960): abstracted in *Wear*, 3: 408 (1960).
227. H. Halliwell, Radiotracers Reveal Engine Wear During Detergent Oil Filtration Study, *S.A.E. Trans.*, 68: 288-297 (1960).
228. B. A. Robbins, P. L. Pinotti, and D. R. Jones, The Use of Radioactive Tracer Techniques to Determine the Effect of Operating Variables on Engine Wear, *ibid.*, pp. 298-304.
229. E. S. Starkman, A Radioactive Tracer Study of Lubricating Oil Consumption, *ibid.*, 69: 86-100 (1961).
230. *Program of the Fourth Japan Conference on Radioisotopes, Tokyo, 1961*, Cosponsored by: Japan Atomic Industrial Forum and Japan Radioisotope Association, Japan Atomic Industrial Forum, Inc., Tokyo, 1961.
231. N. Wada and H. Maeda, Activation of Piston Rings by Plating with Radiochromium, Abstract E-21, Fourth Japan Conference on Radioisotopes, Tokyo, 1961.
232. K. Tamura et al., The Measurement of Blanking Tool Wear by Means of Radioisotopes, Abstract E-22, *ibid.*
233. P. P. Kazlauskas, D. R. Ferris, and W. R. Herfurth, Engine Wear Reduced by Air Flow Control, *S.A.E. J.*, 69(9): 78-80 (1961).
234. J. J. Martin and H. A. Williams, Testing Compression Ring Wear, *ibid.*, 69(7): 68-70 (1961).
235. P. L. Pinotti, P. V. Garin, and D. R. Jones, Radioactive Tracer Research Shows How to Save on Maintenance in Diesel Locomotives (an extract from Radioactive Rings Solve Wear Problems in Diesel Locomotives, presented at S.A.E. Summer Meeting, 1961), *ibid.*, 69(9): 36-37 (1961).
236. R. B. Price, D. N. Sunderman, A. W. Carey, Jr., W. S. Diethorn, and N. J. Beck, Radiotracer Study of Piston Rings and Cylinder Liner: Wear in a Diesel Engine, *Lubrication Eng.*, 18: 56-63 (1963).
237. J. J. Gumbleton, Piston Ring and Cylinder Wear Measurements Illustrate the Potential and Limitations of Radioactive Technique, *S.A.E. Trans.*, 70: 333-349 (1961).
238. J. Kohl, R. D. Zentner, and H. R. Lukens, *Radioisotope Applications Engineering*, D. Van Nostrand Company, Inc., New York, 1961.
239. Radioisotopes in World Industry—Abstracts of Selected Foreign Literature, USAEC Report TID-6613, January 1961, covering OID cards 1 through 725.
240. Radioisotopes in World Industry—Abstracts of Selected Foreign Literature, USAEC Report TID-6613(Suppl. 1), June 1961, covering OID cards 726 through 1300.
241. Radioisotopes in World Industry—Abstracts of Selected Foreign Literature, USAEC Report

TID-6613(Suppl. 2), January 1962, covering OID cards 1301 through 1900.

242. Radioisotopes in World Industry — Abstracts of Selected Foreign Literature, USAEC Report TID-6613(Suppl. 3), October 1962, covering OID cards 1901 through 2475.
243. Radioisotopes in World Industry — Abstracts of Selected Foreign Literature, USAEC Report TID-6613(Suppl. 4), July 1963, covering OID cards 2476 through 3100.
244. R. Wilputte, Studying the Wear of an Engine with Radioactive Tracers (in French), *Ind. Chim. Belge*, 23(12): 1373-1377 (1958). See also Ref. 239, Abstract 351, and OID card 93.
245. H. Stoll, Wear Tests with Radioactive Piston Rings (in German), *Motortech. Z.*, 19(2): 41-44 (1958). See also Ref. 239, Abstract 357, and OID card 57.
246. V. I. Golov, The Activation of Engine Piston Rings with Radioactive Zinc by the Hot Zinc Plating Method (in Russian), *Avtomob. Prom.*, 12: 39-40 (1958). See also Ref. 239, Abstract 367, and OID card 257.
247. G. H. Propstl, The Wear of Piston Rings in Motors (in German), *Dechema*, 30(425): 220-237 (1958). See also Ref. 239, Abstract 355, and OID card 464.
248. D. M. Tarasendo, The Use of Radioisotopes for Investigating the Wear of High-Precision Machinery (in Russian), *Priborostroenie*, 2: 141-149 (1958). See also Ref. 239, Abstract 375, and OID card 105.
249. B. Colding, Testing Machinability by Radioactive Methods, *Acta Polytech. Scand., Mech. Eng. Ser.*, 1: 1-73 (1958). See also Ref. 239, Abstract 365, and OID card 220.
250. M. Smorodinov, The Use of Radioisotopes for Studying the Wear of Machinery Used in Quarrying Building Stones (in Russian), *Stroit. Materialy*, 4(12): 34-36 (1958). See also Ref. 239, Abstract 373, and OID card 274.
251. M. Arkuszewski, Study of the Wear of Machine Parts by Using Radioactive Isotopes (in Polish), *Nukleonika*, 3(4): 382-400 (1958). See also Ref. 239, Abstract 364, and OID card 69.
252. E. Broda, Application of Labeled Atoms in Industry (in Bulgarian), *Tezhka Promishlenost*, 7(6): 13-18 (1958). See also Ref. 239, Abstract 2, and OID card 109.
253. A. I. Nisnevich, The Application of Scintillation Counters for Studying Wear Processes (in Russian), *Zavodsk. Lab.*, 24(8): 971-974 (1958); see Ref. 261. See also Ref. 239, Abstract 372, and OID card 123.
254. D. G. Tochilnikov, Calculation of Wear Resistance in Investigations with Labeled Atoms (in Russian), *Zavodsk. Lab.*, 24(8): 965-971 (1958). See also Ref. 239, Abstract 376, and OID card 462.
255. H. Haga and S. Nagata, Lubrication Characteristics of Aromatic Compounds by Radioactive Tracer Method, *Tech. Rpt. Osaka Univ.*, 8(321): 353-361 (1958). See also Ref. 239, Abstract 359, and OID card 59.
256. S. Nagada, H. Haga, and Y. Tomoda, A Study of the Wear Reduction of Aromatic Compounds Using Radioactive Tracers (in Japanese), *Aisotopu Kenkyu Riyo Soran*, pp. 103-106 (1956). See also Ref. 239, Abstract 361, and OID card 188.
257. R. Gerwin, Atomic "Sleuths" of Technology (in German), *Ind.-Rundschau*, 14(4): 45-46 (1959). See also Ref. 239, Abstract 354, and OID card 35.
258. K. N. Magarik and S. S. Nikolskii, An Automatic Scintillation Counter for Investigating the Wear of Mechanisms (in Russian), *Zavodsk. Lab.*, 25(12): 1512-1515 (1959). See also Ref. 240, Abstract 311, and OID card 1014.
259. M. I. Smorodinov, A Method of Studying Wear by Using Radioisotopes (in Russian), *Zavodsk. Lab.*, 25(7): 875-876 (1959). See also Ref. 240, Abstract 313, and OID card 902.
260. Ta-c. Hsiung et al., Research on the Wear of Cutting Tools Using Radioisotopes (in Chinese), *K'o Hsueh T'ung Pao*, 17: 556-558 (September 1959). See also Ref. 239, Abstract 352, and OID card 137.
261. A. I. Nisnevich, Measurement of Radioactivity of Liquids by Scintillation Counters — Diesel Wear (in Russian), *Zavodsk. Lab.*, 26(2): 175-177 (1960); translated in *Ind. Lab.*, 26(2): 185-186 (December 1960). See also Ref. 241, Abstract 355, and OID card 1729.
262. D. Pavelescu et al., A Method for Studying the Wear of Bearings with Radioisotopes (in Rumanian), *Studii Cercetari Mecanica Aplicata*, 11(6): 1397-1409 (1960). See also Ref. 241, Abstract 353, and OID card 1517.
263. H. Lachmann, Wear Research and Measurement of Machine Parts with Radioisotopes (in German), *Technik*, 15(1): 31-34 (1960). See also Ref. 240, Abstract 308, and OID card 1011.
264. J. Fodor, G. Keomley, and L. Maroti, The Application of Radioisotopes in Wear Testing (in Hungarian), *Energiâ Atomtech.*, 13(12): 563-570 (1960). See also Ref. 241, Abstract 351, and OID card 1401.
265. A. I. Nisnevich and V. I. Sinitsyn, The Use of Radioisotopes for Solving the Problem of Increasing the Service Life of Machine Parts and Mechanisms (in Russian), *Inzh.-Fiz. Zh.*, 3(11): 113-119 (1960). See also Ref. 241, Abstract 401, and OID card 1414.
266. S. V. Rumiantsev, The Use of Radioisotopes and Nuclear Radiation in Machine Building (in Russian), *At. Energ.*, 9(3): 231-233 (1960), [translated as JPRS :6804. See also Ref. 241, Abstract 402, and OID card 1456.
267. P. Daudel, *Radioactive Tracers in Chemistry and Industry* (translated from French by U. Eisner),

Chap. 5: Industrial Applications, pp. 154-191, Charles Griffin & Company, Ltd., London, 1960. See also Ref. 241, Abstract 352, and OID card 1808.

268. T. Sata, K. Abe, and K. Nakajima, Study on Wear in the Shearing Process by Means of Irradiated Tools, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 54(3): 307-312 (1960). See also Ref. 240, Abstract 309, and OID card 1135.

269. Y. Fujii and M. Hirano, Studies on Tool Wear Using Activated Carbide Tools: The Effect of Cutting Oil (in Japanese), *Shizuoka Univ., Rept. Faculty Eng.*, 10: 11-14 (1960). See also Ref. 241, Abstract 352, and OID card 1782.

270. E. P. Nadeinskaia, Investigating the Wear Resistance of Face Milling Cutters by Using Radioisotopes (in Russian), *Vestn. Mashinostr.*, 40(1): 62-67 (1960); translated in *Russ. Eng. J.*, 40(1): 48-52 (1960). See also Ref. 241, Abstract 354, and OID card 1824.

271. S. Popov, Comparing Two Methods for Measuring Tool Wear, *Nucleonics*, 19(12): 76, 78-80 (1961).

272. N. F. Kazakov, *The Use of Radioisotopes for Investigating Cutting Tool Wear* (in Russian), Mashgiz, Moscow, 1960. See also Ref. 242, Abstract 333, and OID card 2134.

273. W. Kaspar-Sickermann, Wear Tests on Piston Rings with Radioisotopes (in German), *Korntechnik*, 3(7): 301-303 (1961). See also Ref. 242, Abstract 327, and OID card 2200.

274. G. Monnot, L. Pons, and J. Thiery, A Study of the Wear of Injection Systems with Radiotracers (in French), *Rev. Inst. Franc. Petrole*, 16(5): 621-629 (1961). See also Ref. 242, Abstract 326, and OID card 2312.

275. D. Pavelescu, I. Iliuc, and S. Barbul, A Study on a Radioactive Method for Estimating the Lubricating Qualities of Compound Oils by Using the Wear of Surfaces, *Rev. Mechan. Aplig.*, 6(4): 539-547 (1961); see Ref. 204. See also Ref. 242, Abstract 332, and OID card 2159.

276. V. S. Lapatukhin and Yu. M. Ovchinnikov, The Application of Phosphorus-32 Isotope for Investigating the Change in Composition in the Film and Wear Resistance of Phosphate Coatings (in Russian), *Zh. Prikl. Khim.*, 34(5): 1002-1007 (1961). See also Ref. 242, Abstract 334, and OID card 2323.

277. Ch-l. Liu, New Progress in Research on Wear Using Radioisotopes (in Chinese), *K'o Hsueh T'ung Pao* (Science Bull.), 11: 30-33 (1961). See also Ref. 242, Abstract 323, and OID card 2226.

278. Z. Turek and J. Cesanek, The Application of Radioisotopes in Research on Cutting Tools (in Czechoslovakian), *Strojirenstvi*, 11(9): 682-688 (1961). See also Ref. 242, Abstract 325, and OID card 2253.

279. J. Kieszniewski et al., A Direct Radioisotope Method of Investigating the Wear of Wire Drawing Dies: Parts 1 and 2, *Wire Industry*, 28(334): 991-993 (October 1961); 28(335): 1111-1116 (November 1961). See also Ref. 242, Abstract 331, and OID card 2169.

280. H. Ramdohr, Abrasion Tests on High-Speed Ball Bearings (in German), *Kerntechnik*, 3(1): 19-21 (1961). See also Ref. 241, Abstract 397, and OID card 1400.

281. J. Michalowska, The Use of Radioactive Tracers for Examining the Oiliness of Mineral Oils (in Polish), Report R-41, in *Symposium on Isotopes and Techniques, Warsaw, 1961.* See also Ref. 243, Abstract 380, and OID card 2613.

282. A. Pradzynski and W. E. Wajnsztejn, An Investigation of the Wear of Bearings in the Presence of Abrasive Particles Using Radioisotopes (in Polish), Report R-37, in *Symposium on Isotopes and Techniques, Warsaw, 1961.* See also Ref. 243, Abstract 341, and OID card 2610.

283. Z. Banasik, A Device for Continuous Wear Measurements Using Radioisotopes (in Polish), Report R-46, in *Symposium on Isotopes and Techniques, Warsaw, 1961.* See also Ref. 243, Abstract 342, and OID card 2618.

284. Y. Horiguchi and I. Okawa, Fundamental Studies on Metal Wear Using Radioisotopes (in Japanese), *J. Metal Finishing Soc. Japan*, 13(5): 193-197 (1962). See also Ref. 243, Abstract 340, and OID card 2869.

285. T. Saitoh, A Radioactive Method for Measuring Engine Deposits (in Japanese), *Bull. Sci. Eng. Res. Lab., Waseda Univ.*, 19: 38-44 (1962). See also Ref. 243, Abstract 125, and OID card 2872.

286. D. Pavelescu and I. Iliuc, A Method for Measuring the Thickness of Lubricating Oil Films (in Rumanian), *Met. Constructia Masini*, 14(6): 553-559 (1962); see Ref. 204. See also Ref. 243, Abstract 176, and OID card 2892.

287. K. Kollmann and D. Stegemann, The Application of Radioisotopes to Research Tasks in Engineering (in German), *Kerntechnik*, 4(2): 41-44 (1962). See also Ref. 243, Abstract 336, and OID card 2570.

288. G. Oswald, The Methodology of Wear Measurement (in German), *Isotopen Tech.*, 2(1): 7-11 (1962). See also Ref. 243, Abstract 334, and OID card 2652.

289. A. Filip, The Application of Radioisotopes in Studying the Wear of Machine Parts (in Serbo-Croatian), *Tehnika*, 17(1): 24b-h (1962). See also Ref. 243, Abstract 352, and OID card 2817.

Use of Radioisotopes in the Foreign Coal Industry

290. *a.* H. J. Rose, Potential Applications of Radioisotopes to the Mining, Transportation, Storage, Handling, and Use of Coal, USAEC Report NYO-2859, Bituminous Coal Research, Inc., Nov. 1, 1960.

b. Ibid., Implications of Radioisotopes to the Mining Industry, presented at Conference on Radioisotopes in the Mining Industry, Denver, April 13–14, 1961, American Mining Congress, Washington, D. C.

291. Technology Fights Water Pollution, *Chem. Eng. News*, 40(53): 55-59 (Dec. 31, 1962); coal discussed on pp. 56-58.

292. V. G. Segalin, The Use of Radioisotopes for Automation in the Coal Industry (in Russian), Gosgortekhizdat, Moscow, 1960. See USAEC Report TID-6613(Suppl. 2), Abstract 372a.

293. H. Fushimi, Utilization and Application of Radioisotopes in Mining (in Japanese), *Sentan* (Coal Preparation Review, Japan), 8: 277-284, 321-325 (1958); 9: 130-132, 169-175, 260-263, 308-315 (1959). See USAEC Report TID-6613(Suppl. 1), Abstracts 326 and 327.

294. G. Milde, Use of Radionuclides for Hydrogeological Mining Investigations (in German), *Isotopen Tech.*, 2: 328-335 (1962).

295. N. V. Glazov, The Adaptation of Radioactive Isotopes to Engineer Research, Gosatomizdat, Moscow, 1962. See USAEC Translation AEC-tr-5525.

296. Zh. M. Kanlybaeva, A New Method of Mine Surveying Based on the Use of Radioisotopes (in Russian), *Vestn. Akad. Nauk Kaz., SSR*, 14(9): 66-72 (1958). See USAEC Report TID-6613, Abstract 403.

297. Yu. P. Bulashevich, E. P. Didenko, I. N. Sen'ko-Bulatnyi, and A. P. Fisenko, Radioactive Core Sampling in Coal Deposits, in *Proceedings of the All-Union Scientific and Technical Conference on the Application of Radioactive Isotopes, Moscow, 1957, Prospecting and Mining of Useful Minerals*, pp. 29-38 (in Russian).

298. Yu. P. Bulashevich, G. M. Voskoboinikov, and L. V. Muzyukin, Nuclear Geophysics in Prospecting for Ore and Coal Deposits (in Russian), in *Proceedings of the Conference on the Use of Radioisotopes in the Physical Sciences and Industry, Copenhagen, 1960*, Report STI/PUB/20, Vol. 1, pp. 101-116, International Atomic Energy Agency, Vienna, 1962. See Preprint RICC/309 and USAEC Translation AEC-tr-4412.

299. Use of Atomic Energy in Coal Mines. The Construction of a Gamma-Ray Gage (in Chinese), *Mei T'an Kung Yeh* (Coal Industry), 14: 8 (July 1958). See USAEC Report TID-6613(Suppl. 1), Abstract 323.

300. V. G. Segalin and A. A. Rudanovskii, Use of Radioactive Isotopes for the Automation of Mining-Sinking Machines, in *Proceedings of the All-Union Scientific and Technical Conference on the Application of Radioactive Isotopes, Moscow, 1957, Machine Building and Instrument Making*, USAEC Translation AEC-tr-4492, pp. 170-172.

301. M. L. Gol'din, Review of the Use of Radioactive Isotopes in the Ore-Concentration and Mining Industry (from All-Union Conference on the Introduction of Radioactive Isotopes and Nuclear Radiation into the National Economy of the USSR) (in Russian), *At. Energ.*, 9: 225-226 (1960); English translation in *Soviet J. At. Energ.*

302. A. V. Chashchinov, Work of the "Krasnyi Metallist" Plant on Manufacturing and Industrial Utilization of Gamma Relays for Automation of the Coal Industry, in *Radioactive Methods of Control and Regulation of Industrial Processes, Transactions of Scientific-Technical Conference, Riga, 1957*, USAEC Translation AEC-tr-4139, pp. 173-181.

303. Ye. Ye. Rubinovich, Concerning the Use in the Coal Industry of Semiconductor Triodes in Automation and Monitoring Apparatus Based on the Utilization of Radioactive Radiations, *ibid.*, pp. 207-213.

304. M. B. Neiman, Radioisotopes and Their Application, Vses. obshchestvo po rasprostraneniyu politicheskikh i nauch. znanii (in Russian), *Izdatel'stvo Znanie*, Ser. 9, No. 13, Moscow, 1959. See USAEC Report TID-6613, Abstract 45.

305. J. W. Haffner and D. Oestreich, Literature Survey on World Isotope and Radiation Technology, USAEC Report ARF-1194-13, Armour Research Foundation, June 30, 1962.

306. I. M. Verhovskii et al., Use of a Gamma-Location Method to Study the Jigging Process (in Russian), *Gorn. Zh.*, 1: 53-56 (January 1958). See USAEC Report TID-6613, Abstract 406.

307. V. D. Goroshko, Investigation of the Attenuation of Gamma-Rays Passing Through Coal (in Russian), *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk, Met. i Toplivo*, 1: 120-122 (1959). See USAEC Report TID-6613, Abstract 402.

308. V. G. Segalin, Utilization of Penetrating Radiations for the Automation of Coal Concentration Processes, in *Radioactive Methods of Control and Regulation of Industrial Processes, Transactions of Scientific-Technical Conference, Riga, 1957*, USAEC Translation AEC-tr-4139, pp. 152-172.

309. A. A. Rudanovskii, Use of the Method of Induced Radioactivity for Automation of Rock Separation, *ibid.*, pp. 138-151.

310. H.-K. Bothe and H. Langer, Measurement of the Local Velocity of Brown Coal in Tube Driers by Means of Radioactively Labeled Coal Particles (in German), *Isotopen Tech.*, 1: 11-13 (1960).

311. I. L. Liplavk and E. P. Boliter, Radiometric Methods of Determining the Degree of Coal Mixing (in Russian), *Zavodsk. Lab.*, 25: 1079-1081 (1959).

312. E. P. Boliter, N. S. Gryaznov, and P. I. Shashmurin, Radiography of Coal (in Russian), *Dokl. Akad. Nauk SSSR*, 134: 1403-1405 (1960).

313. K. P. Medvedev and V. M. Petropol'skaya, Theoretical and Experimental Bases for the Application of Radioisotopes to the Investigation of

the Processes of Thermal Decomposition and Fusion of Coal (in Russian), *Koks i Khim.*, 3: 25-29 (March 1958). See USAEC Report TID-6613, Abstract 404.

314. K. Irmer, Measurement and Control with Radioisotopes in the Brown Coal Industry (in German), *Bergbautechnik*, 10(5): 247-251 (1960). See USAEC Report TID-6613(Suppl. 1), Abstract 325.
315. G. Flügge, Use of Radioactive Isotopes in Coal Mining (in German), *Atompraxis*, 4(1): 6-13 (1958).
316. W. Häusler, Application of Radioisotopes in the Fraction of Brown Coal Mining (in German), *Isotopen Tech.*, 1: 155-156 (1961).
317. E. W. Leaver, Some Uses of Radioisotopes in Automation, presented at Canadian Nuclear Association International Conference on Operating Experience and Future Development of Power Reactors and Radioisotopes, Montreal, Canada, May 27–29, 1963.
318. S. Sakai, Application of Radioisotopes to Railway Signal System (in Japanese), *Denki Zasshi (OHM)*, 49(5): 75-78 (May 1962). See OID card 3162.
319. *Minerals Yearbook*, 1961, Vol. II, Fuels, p. 157; also in *Coal Age*, November 1961, p. 37.
320. H. Imamura, J. Tujii, and M. Yokooji, Measurement of the Concentration of Pulverized Coal in a Pneumatic Conveyor Using Beta-Emitting Isotopes, Abstract E-10, Fourth Japan Conference on Radioisotopes, Tokyo, 1961.
321. S. Enomoto, T. Furuta, and C. Mori, Application of X-ray Absorption Analysis Utilizing Radioisotopes to Analyses of Fuels, Fourth Japan Conference on Radioisotopes, Tokyo, 1961, pp. 179-201, USAEC Translation AEC-tr-5614.
322. *a.* N. V. Gorbatyuk, G. Z. Borukhovich, V. V. Parkhomenko, and A. V. Chashinov, Rapid Method for Determining the Ash Content of Coal by Beta-Ray Scattering (in Russian), *Zavodsk. Lab.*, 26: 1094-1096 (1960).
    b. S. A. Bel'skii and E. M. Lobanov, Determination of Ash Content of Coal by Means of Radioactive Isotopes, in *Radioactive Methods of Control and Regulation of Industrial Processes, Transactions of Scientific-Technical Conference, Riga, 1957*, USAEC Translation AEC-tr-4139, pp. 132-137.
323. H. Mori and S. Taira, The Rapid Determination of Ash in Coal by Beta-Ray Backscattering, Abstract E-27, Fourth Japan Conference on Radioisotopes, Tokyo, 1961.
324. E. Dahn, Determination of the Ash Content of Brown Coal by Means of Beta Backscattering (in German), *Isotopen Tech.*, 1: 150-151 (1961).
325. T. Jirkovsky, New Apparatus for Determining Radiometrically the Ash Content of Coal by the Absorption of Gamma Rays (in Czechoslovakian), *Jaderna Energie*, 6(2): 63-64 (1960). See USAEC Report TID-6613(Suppl. 1), Abstract 324.
326. S. Bisztray-Balku, A. Lévai, J. Kakas, M. Nagy, and K. Varga, Determination of the Calorific Value of Coals by the Radiological Method (in Hungarian), *Energia Atomtech.*, 13(6): 472-483 (1960). See USAEC Report TID-6613(Suppl. 2), Abstract 366.
327. H. Fushimi, On the Application of Radioisotopes in Mine Ore Dressing, Abstract T-16 59/P-16, Third Japan Conference on Radioisotopes, Tokyo, 1959.
328. J. Kakas, M. Nagy, K. Varga, A. Bisztray-Balku, and A. Lévai, Determination of the Calorific Value of Coal by Means of Radioactive Radiation (in German), *Isotopen Tech.*, 1: 144-146 (1961).
329. E. Ya. Studnits, Study of Drive Wear in Coal Machines, in *Proceedings of the All-Union Scientific and Technical Conference on the Application of Radioactive Isotopes, Moscow, 1957, Machine Building and Instrument Making*, USAEC Translation AEC-tr-4492, pp. 82-87.
330. H. Fushimi, Application of Radioisotopes in the Basic Test and the Baum Jig Applied Test for Coal (in Japanese), *Sentan* (Coal Preparation Review, Japan), 9: 45-49 (1959). See USAEC Report TID-6613, Abstract 398.
331. *a.* D. W. Van Krevelen, H. I. Waterman, and P. M. Wolfs, Chemical Activity of Carbonization, Investigated on the Polymer Model of Coal. I. Purpose and Method of the Investigation (in German), *Brennstoff-Chem.*, 40: 155-159 (1959). See USAEC Report TID-6613, Abstract 400.
    b. P. M. J. Wolfs, D. W. Van Krevelen, and H. I. Waterman, *ibid.*, II. Structure Analysis by Means of Radiocarbon (in German); III. Synthesis of Models (in German), *Brennstoff-Chem.*, 40: 189-194; 215-219 (1959). See USAEC Report TID-6613, Abstract 401.

Instrument Development

332. R. L. Ely, Jr., and L. F. Ballard, Geiger Counting of Tritium as Water Vapor, USAEC Report ORO-484, Research Triangle Institute, July 1, 1961.
333. V. P. Guinn and C. D. Wagner, A Comparison of Ionization Chamber and Liquid Scintillation Methods for Measurement of Beta Emitters, presented at the Symposium on Ionization Chamber Measurements of Radioactivity and Radiation, San Francisco, November 13, 1959. See also C. D. Wagner and V. P. Guinn, For Low Specific Activity: Use Scintillating Counting, *Nucleonics*, 13(10): 56-59 (1955).
334. R. W. P. Drever and A. Moljk, Measurement of Tritium as Water Vapor, *Rev. Sci. Instr.*, 27: 650-651 (1956).
335. W. F. Merritt, System for Counting Tritium as Water Vapor, *Anal. Chem.*, 30: 1745-1747 (1958).

336. E. B. Butler, Counting Tritiated Water at High Humidities in the Geiger Region, *Nature*, 176: 1262-1264 (1955).

337. J. F. Cameron, Measurement of Tritium in Water Samples, *Nature*, 176: 1264 (1955).

338. C. P. Joshi, On the Temperature Effect in Geiger-Müller Counters, *Indian J. Phys.*, 27: 393-398 (1953).

339. L. Reiffel and N. S. Kapany, Some Considerations on Luminescent Fiber Chambers and Intensifier Screens, USAEC Report ARFDA-24, Armour Research Foundation, 1960; also, L. Reiffel and N. S. Kapany, *ibid.*, *Rev. Sci. Instr.*, 31: 1136-1142 (1960).

340. N. S. Kapany, Fiber Optics. I. Optical Properties of Certain Dielectric Cylinders, *J. Optical Soc. Am.*, 47: 413-422 (1957).

341. G. T. Reynolds and P. E. Condon, Filament Scintillation Counter, *Rev. Sci. Instr.*, 28: 1098-1099 (1957).

342. C. Preston, A Study of the Feasibility of Using Scintillating Fibers for Low Energy Beta Counting, USAEC Report ARF-1192-6, Armour Research Foundation, Feb. 23, 1962.

Section

III

Isotopes and Radiation Technology

Safety

Evaluation of ORNL Cardboard-Box–Steel-Can Shipping Container

By Karl W. Haff*

The ORNL cardboard-box–steel-can containers used for shipping radioisotopes were subjected to a series of tests, proposed by Messenger and Fairbairn[1] of the United Kingdom Atomic Energy Authority, and more recently proposed to the International Atomic Energy Agency (IAEA). The purpose of the tests was twofold: (1) to determine whether these packages meet present IAEA specifications[2] and (2) to evaluate the suggested tests. All proposed tests for type A† containers were made except the vibration and bump tests, for which equipment was not available. The vibration test is considered to be not too important for this kind of package since the cardboard packaging would damp out any vibration, and the bump test seems unnecessarily harsh for packages that are not to be reused. Only the free-drop and fire tests for type B containers were made.

The shipping containers tested were of two sizes: an 8.5-in. cube weighing 3 lb and a 12.25-in. cube weighing 4 lb (Fig. III-1*a*). The boxes are made of cardboard according to U. S. Interstate Commerce Commission (ICC) Specification 12B (Ref. 3) and are closed with metal staples. They contain cardboard spacers, which center a $4\frac{1}{4}$-in.-diameter by $6\frac{7}{8}$-in.-high steel can with a wall thickness of 0.01 in. The can is filled with an absorbent material, Chem-Pac, in the center of which is a glass bottle that in use would contain a radioactive material; in these tests it was filled with water. Three packages of each size were used, being subjected to the tests in the sequence shown in Table III-1.

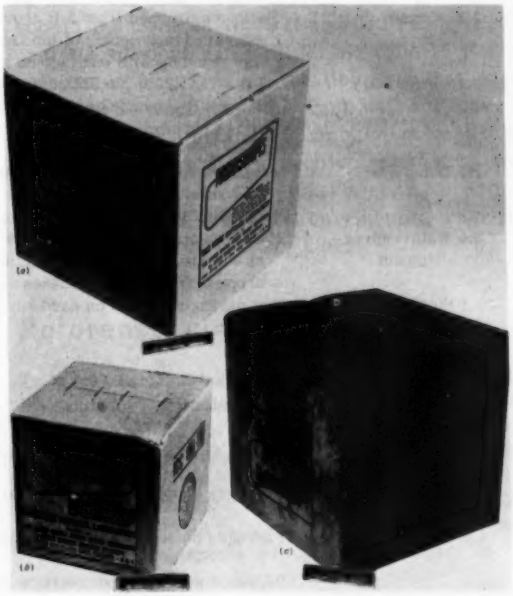

Fig. III-1 Small (8.5 cu in.) cardboard shipping container (*a*) before tests, (*b*) after cold test, and (*c*) after water-spray–impact test. Scales in inches.

Evaluation of Containers

The results (Table III-1) indicated that the subject shipping containers adequately meet IAEA type A requirements. However, the packaging did not withstand type B fire requirements.

*Oak Ridge National Laboratory.

†A type A package is one that will withstand any incident normal to transportation. A type B package is one that will withstand unusual and/or accident conditions not normal to transportation.

Table III-I RESULTS OF TESTS ON ORNL CARDBOARD-BOX–STEEL-CAN SHIPPING CONTAINERS

Test	Description	Results
	Type A	
2.1 Dry heat	Packages in closed chamber; temperature brought to 60°C, relative humidity to 40%, and held 48 hr	No damage
2.2 Cold	Packages in closed chamber; temperature brought to −40°C and held 48 hr; packages removed and subjected to free-drop test (below)	Slight crumbling of corners (Fig. III-1*b*)
3.4 Free drop	Temperature of packages brought back to ambient and packages dropped from 4.5 ft onto two corners and four faces	No damage
3.12 Corner drop	Packages dropped from 5 ft aboveground so that corner struck center of top face of identical package standing with one face on ground	No damage
3.13 Penetration	25-lb bar, 1.25 in. in diameter, rounded end, dropped from 3 ft above floor so that end struck center of top of package	8.5-in. package undamaged; 12.25-in. package penetrated to 1 in.; one package of each size opened, and steel cans undamaged (Fig. III-2)
2.3 Damp heat	Packages subjected to four cycles of: 12 hr at 35°C, 95% relative humidity; and 3.5 hr cooling to 20°C, 5 hr at 20°C, and 3.5 hr heating to 35°C	No damage
2.4 Water-spray–impact	Packages sprayed 20 min from 8-ft distance with H_2O at 30 psig, striking at 45° angle, and packages dropped from 5 ft onto bases	Slight peeling of cardboard at corners (Fig. III-1*c*)
3.1 Stacking	Wet packages placed on hard surface and loaded with 100 lb for 24 hr	8.5-in. package crumpled but did not collapse; 12.25-in. package bent but did not collapse completely; one package of each size opened, and no damage to steel can or bottle (Fig. III-3*a* and *b*)
	Type B	
4.1 Free drop (accident)	Packages dropped from 30 ft onto concrete	No damage (Fig. III-3*c*)
4.2 Fire	Packages placed in furnace for 30 min at 700°C	Metal cans leaked, bottle caps melted, and water in bottles evaporated
	Repeated with ICC Specification 2R* container inside the steel case	Metal cans leaked, bottle caps melted, and water in bottles evaporated

*A metal container which is gasket-sealed to prevent loss of liquid. It was designed primarily to eliminate the absorbent materials that are packed around liquid radioactive shipments to absorb liquid in case of bottle breakage.

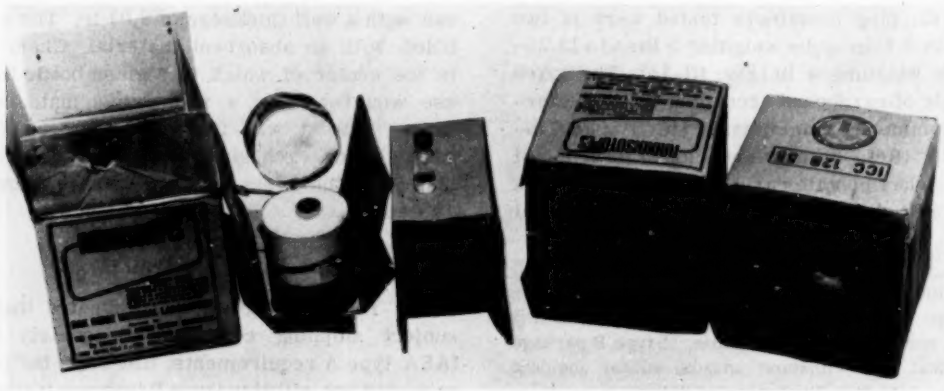

Fig. III-2 Small (8.5 cu in.) cardboard shipping containers after penetration test. Scale in inches.

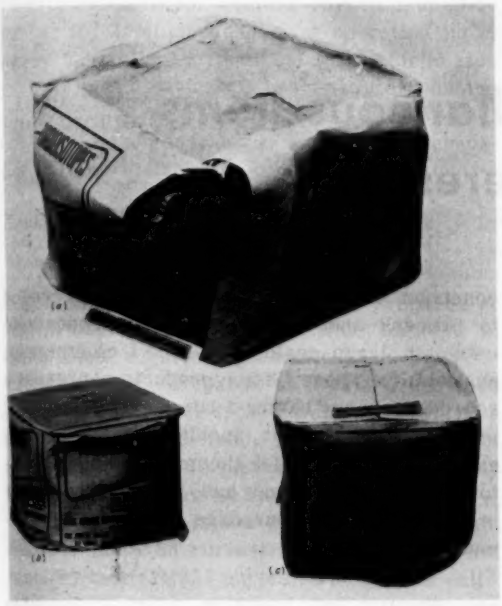

Fig. III-3 Cardboard shipping containers: (*a*) large (12.25 cu in.), and (*b*) small (8.5 cu in.) after stacking test, and (*c*) small container after free-drop test. Scales in inches.

Evaluation of Tests

Although the proposed tests appear reasonable, most of them could be eliminated if current U. S. ICC specifications[3] for package construction were used, since in most cases appropriately approved ICC packages will also meet IAEA specifications. In the few cases where additional specifications are required, they should be written in terms of performance specifications rather than as specific tests. Specific comments on the tests are:

1. The type A free-drop (accident), penetration, and water-spray–impact tests are entirely satisfactory.

2. The type A dry heat, cold, and damp heat tests are unnecessary; material that meets the stacking, drop, and spray tests will also meet the former. Other possible failures are freezing, which is not covered by any of the tests, and ungluing, which could be detected by using warm water for the water-spray test.

3. The type A corner drop test could be combined with the water-spray test to serve as the impact part of that test.

4. The type B free-drop test (accident) should obviate all other structural tests for type B packages except lifting-point requirements. It is also felt that the 30-ft free-fall requirement should be changed to 15 ft as required by Federal Regulations (10 CFR 72.5). (The 15-ft requirement is based on the premise that cask tie-down is such that the cask will not leave a vehicle at greater than 30 mph upon impact of the vehicle and that any object struck by the cask will absorb half the total energy.)

5. The type B fire test is only 30 min, whereas the standard U. S. test[4] is 1 hr.

References

1. W. de L. M. Messenger and A. Fairbairn, The Transport of Radioactive Materials. Interim Recommendations for the Applications of Environmental Tests to the Approval of Packaging, British Report AHSB (S) R 19, Part D, Appendix N.
2. Regulations for the Safe Transport of Radioactive Materials. IAEA Safety Series, No. 6; *ibid.*, Notes on Certain Aspects of the Regulations, No. 7, pp. 76, 112, IAEA, Vienna, 1961.
3. T. C. George, Agent, Tariff No. 13, Interstate Commerce Commission, Regulations for Transportation of Explosives and Other Dangerous Articles by Land and Water in Rail Freight Service and by Motor Vehicle (Highway) and Water Including Specifications for Shipping Containers, 1960, (*a*) Specification 12B, Fiberboard boxes, 78.205 through 18, pp. 282-285; (*b*) Specification 2R, inside containers, metal tubes, 78.34-1 through 4, p. 161.
4. Methods of Fire Tests of Building Construction and Materials, ASTM Standard E-119-61, 1961.
5. Title 10, *Code of Federal Regulations*, Part 72, Regulation To Protect Against Radiation in the Shipment of Irradiated Fuel Elements, *Federal Register*, September 1961.

Section

IV

Isotopes and Radiation Technology

Miscellaneous Items of Interest

Half-Million Curies of Cerium-144 Arrives in Oak Ridge

A half-million curie shipment of Ce^{144}—the largest shipment ever received in a single container—arrived in Oak Ridge in March. The shipment originated at the AEC's Hanford Works at Richland, Wash., and was shipped in a specially designed, heavily shielded cask being used routinely for shipment of bulk amounts of radioisotopes from Richland to Oak Ridge. After further purification in the Fission Products Development Laboratory at ORNL, the cerium will be used in the AEC programs for development of radioactive sources for isotopic power and radiation applications. Cerium-144 is one of several radioisotopes that can be separated at Hanford during the chemical processing of irradiated fuel slugs used in the plutonium production reactors there.

Private Industry Considers Take-Over of Hanford Fission-Product Recovery Plant

More than 50 industrial representatives from 22 interested firms attended a two-day meeting in Oak Ridge, March 17 and 18, to obtain additional technical details on the purification and fabrication of fission-product sources. An earlier meeting was held in Richland, Wash., in February. These meetings followed Chairman Glenn T. Seaborg's announcement late in January that the AEC is inviting expressions of interest from industry concerning industrial participation in a large-scale fission-product recovery program at the AEC's Hanford Works near Richland.

The overall program includes recovery of fission products such as Sr^{90}, Ce^{144}, Cs^{137}, and Pm^{147} from wastes generated at Hanford during operation of the plutonium production reactors. The AEC proposes to ask private industry to construct and operate the new facilities needed to process and encapsulate these products to establish large-scale, low-cost commercial availability. These fission products represent a source of energy having a commercial potential in a number of fields, including such uses as radioactive sources for thermoelectric generators for use on land and in space, and for process radiation purposes such as the pasteurization of food.

First Nuclear-Powered Deep-Sea Weather Station Begins Operations in Gulf of Mexico

A Sr^{90} nuclear generator for supplying electric power for a Navy unmanned weather station went into unattended operation in February near the center of the Gulf of Mexico. Designed for a 10-year lifetime, the 60-watt generator is the first of its kind to power a deep-sea anchored automatic weather station by nuclear energy and replaces batteries that require costly and often hazardous recharging every six months. The generator, designated SNAP-7D, was developed for the AEC by the Nuclear Division of the Martin Company, Baltimore, and was fueled by the AEC's Oak Ridge National Laboratory.

The nuclear device is 22 in. in diameter, $34\frac{1}{2}$ in. high, and weighs about 4600 lb, including shielding, and is fueled with about 20 lb of insoluble strontium titanate. A special high-strength corrosion-resistant metal, Hastelloy C, encases the 14 fuel capsules, forming a seal designed to last 500 years—a period in which the radioactivity will have decayed to a very small fraction of the original amount.

Heat from the decaying fuel is continuously converted into electricity through 120 pairs of thermocouples which surround the fuel, and this electricity is stored in batteries. It is then

readily available for weather-data transmission during its 2 min and 20 sec of operation out of every 3 hr. Power from the generator is also used to light a navigation beacon to alert passing ships. Since no moving parts are involved, nothing in the generator is subject to mechanical failure.

Brookhaven Receives 215,000 Curies of Cesium-137 for Food Sterilization

The largest Cs^{137} source ever prepared at ORNL has been shipped to BNL for use in irradiation engineering studies. The 215,000-curie source, prepared at ORNL's Isotopes Development Center from atomic waste products originally shipped from Hanford, is the first source prepared for use in the High Intensity Radiation Development Laboratory.

The source consists of 48 elements of cesium chloride (200,768 curies) and nine elements of cesium glass (14,225 curies). The cesium chloride units were prepared by pressing dry cesium chloride powder in tool steel dies at 50,000 psi. Each unit contains 11 rectangular blocks 1 in. by $\frac{1}{4}$ in. in size.

The cesium glass was made by placing a dry mixture of cesium carbonate, silicon dioxide, and various additives in a graphite mold and melting it in a furnace under nitrogen pressure.

Both the chloride and glass units were sealed within two welded rectangular stainless-steel containers.

Highly Enriched Calcium-46 Available from ORNL

Calcium-46, enriched to >40% from a natural abundance of 0.003%, is now available from ORNL. Of particular interest is the fact that the Ca^{46}/Ca^{44} ratio is ~15:1 (compared to the ~1:600 ratio of normal calcium), which makes the material very desirable target material for Ca^{47} production by the $Ca^{46}(n,\gamma)Ca^{47}$ reaction. The Ca^{47}/Ca^{45} ratio in the radioproduct is >100:1, which makes it quite suitable for both diagnostic and therapeutic applications. The price of the Ca^{46}, inventoried as $CaCO_3$, is $635 per milligram of contained calcium.

AEC Withdraws from Production of Five More Isotopes

Following a request by the Nuclear Science and Engineering Corporation (NSEC), the AEC, in accordance with its general policy to discontinue providing material or services that are reasonably available from commercial sources, announced planned withdrawal from production of five radioisotopes: Cr^{51}, Fe^{55}, Co^{58}, Cs^{134}, and Ce^{141}. This new action affects primarily the Oak Ridge National Laboratory, chief producer of most of the AEC isotopes. Approximately 90 days will be allowed for the transition from Commission-sponsored production to commercial suppliers of these radioisotopes after the latter have announced satisfactory price and scheduling information. This follows the withdrawal from production of I^{125} and I^{131} (except when higher quality fission-product material is required) reported in the Winter 1963–1964 issue of *Isotopes and Radiation Technology*.

It is expected that similar action on a few other isotopes will soon follow. NSEC had also asked the AEC to withdraw from producing and selling Mn^{54}, which the AEC says it does not yet produce or sell, and Sr^{85}, which the AEC says it can sell at a price considerably lower than NSEC proposes.

New Sealed-Source Regulations Proposed

AEC is proposing an amendment to the present regulations governing the testing requirements for devices which contain sealed radioactive sources and are used in measuring and controlling equipment operated under a general AEC license [see *Isotopes and Radiation Technology*, 1(2): 160-174]. At present the sources as well as the on-off mechanisms and indicators must be tested every six months for leaks and proper operation. The proposed amendment would change this to testing once during the period between the third and sixth month following installation, with subsequent test intervals of six months to three years as authorized after evaluation of design features. An industry advisory conference was held on March 11 at the AEC Division of Licensing and Regulation offices in Bethesda, Md., to obtain industry's views on the proposal.

AEC Makes Radioisotope Customer Lists and Production Technique Manuals Available

Lists of ORNL, BNL, and Mound Laboratory radioisotope customers were distributed in early January to all commercial isotope suppliers and distributors in the United States.

Manuals on all radioisotope production techniques developed by ORNL, BNL, and Mound Laboratory are being prepared for distribution at the June 11–12 AEC information meeting with industry on radioisotope production technology being used by the national laboratories. This meeting will be held in the AEC auditorium in Germantown, Md.

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